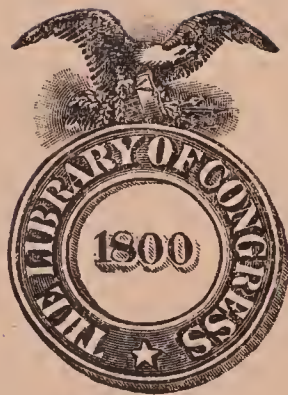


**BRIEF COURSE
IN CHEMISTRY**

NEWELL

D. C. HEATH & COMPANY

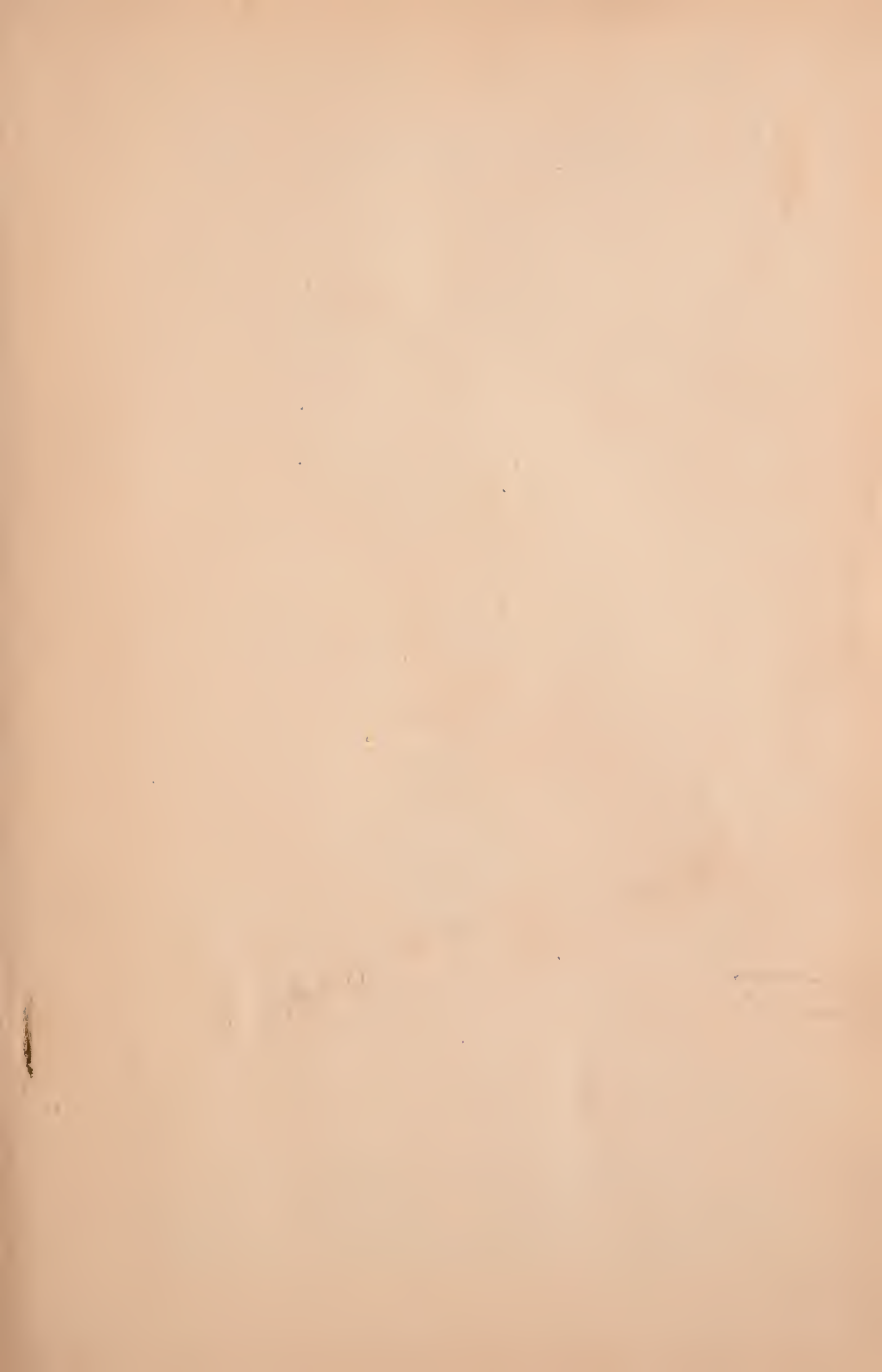


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A BRIEF COURSE IN CHEMISTRY

BY

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AUTHOR OF

EXPERIMENTAL CHEMISTRY, DESCRIPTIVE CHEMISTRY,
GENERAL CHEMISTRY, PRACTICAL CHEMISTRY,
LABORATORY EXERCISES FOR A
BRIEF COURSE IN CHEMISTRY

PART I — MINIMUM ESSENTIALS

PART II — SUPPLEMENTARY TOPICS



D. C. HEATH AND COMPANY

BOSTON NEW YORK CHICAGO LONDON
ATLANTA SAN FRANCISCO DALLAS

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PREFACE

THIS book contains the text for a brief course in chemistry. The subject matter is limited to the topics for a minimum course in chemistry selected by a Committee of the American Chemical Society.

The book consists of two parts. Part I contains the essential topics only. Part II contains supplementary topics.

Part I, about 225 pages of actual text, with nearly 150 illustrations, includes the topics selected by the Committee as essential for a brief course in chemistry. These are the basal topics needed for any course, whatever the kind of school, the aim of the teacher, or the goal of the pupil.

Part II, about 125 pages of text, with 85 illustrations (some full page), includes the supplementary topics selected by the Committee as suitable for special needs and additional study. These topics are intended solely to supplement the essential topics in Part I. The wide range of topics provides material for extending or developing a course adapted to local needs, to special fields, or to the future work of the pupil.

Parts I and II are linked in two ways. First, the sections throughout the book are numbered consecutively and the topics are connected wholly or in part by numerous cross references. Second, at the end of most chapters in Part I there are references by number and title to supplementary sections in Part II. Hence the minimum essentials can be readily and appropriately extended by the supplementary topics.

The EXERCISES and PROBLEMS at the end of the chapters and of many topics have been carefully chosen. Teachers are urged to use these adjuncts to drive home facts and principles not readily learned in other ways.

No course in chemistry, however brief, is effective without correlated laboratory work. Experiments for this course are in the author's **LABORATORY EXERCISES FOR A BRIEF COURSE IN CHEMISTRY**. This laboratory manual consists of the experiments selected by the Committee of the American Chemical Society, together with supplementary experiments for the pupil and demonstration experiments for the teacher. References by number and title at the end of the chapters and of certain topics in the textbook show the experiments in the laboratory manual needed for the brief course.

The ample **INDEX** will permit teachers to follow up special topics or concentrate on certain fields.

The books listed in the **APPENDIX** will enable teachers to add interest to their courses and to show the service of chemistry to the home, the community, and the nation.

LYMAN C. NEWELL

BOSTON, MASS.
April, 1929

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BRIEF COURSE IN CHEMISTRY

PART I

MINIMUM ESSENTIALS

BRIEF COURSE IN CHEMISTRY

CHAPTER I

THE FIELD OF CHEMISTRY — WHAT CHEMISTS DO

1. The field of chemistry. — The field of chemistry is vast. Food, clothing, wood, metals, air, water — all these and many more are related directly or indirectly to chemistry.

Every industry, large or small, involves chemistry in some way. In some industries chemicals are made — acids, alkalies, dyes, solvents, bleaching substances, disinfectants, and photographic materials. In other industries iron, steel, glass, cement, medicines, and fertilizers are manufactured. In still others metals are extracted from ores, gasoline is distilled from petroleum, gas and coke are made from coal, rubber is prepared from the sap of certain trees, wood is transformed into paper, and cotton is made into rayon and explosives. In special industries chemicals are used in many processes, *e.g.*, in grinding, polishing, filtering, washing, settling, drying, bleaching.

In the home, chemistry is used in cooking and cleaning, in providing water, gas, light, and heat, in protecting our houses from the weather.

On the farm, chemistry is applied in the fertilizers, which are put into the ground to make crops grow, in the insecticides which are sprayed on trees and plants to kill pests.

In the community, chemistry plays an important part in guarding the water supply, enforcing food and health laws,

CHAPTER II

SCOPE OF A BRIEF COURSE — SUBSTANCES — PROPERTIES — CHEMICAL CHANGE

3. What we study in a brief course in chemistry. — In a brief course in chemistry we limit our study to the properties and uses of certain substances and the changes involved in important chemical processes. And since chemistry is one of the sciences, we study a few laws and theories which summarize and interpret facts. In addition we study some practical application of chemistry illustrated by the manufacture and utilization of substances related to our daily life.

4. Substances. — In every-day language a substance is almost any kind of material. Thus, soil, flour, and water are substances. In chemical language, a **substance** is a special kind of material which is alike throughout. For example, sulfur is a substance, because each particle of pure sulfur is alike. Similarly, water, sugar, iron, sulfuric acid, salt, and aluminum are substances. Not all the materials used in chemistry consist of a single substance. Soil, for example, contains several different substances, and a chemist in describing soil would say it consists of such single substances as sand, water, organic matter, clay, and limestone (see § 12).

5. Properties. — Every substance has characteristics called **properties**. And if we know or learn some of these properties, we can recognize, identify, or describe the substance.

6. Physical properties. — Some properties are readily detected by observation, *e.g.*, color, odor, taste, hardness, solubility, luster, and physical state (solid, liquid, or gas), while other properties need special apparatus for their

detection, *e.g.*, melting point, boiling point, conductivity of heat and electricity, crystal form, ease of liquefaction or solidification, and relative weight (*i.e.*, whether lighter or heavier — and how much — than some standard such as air or water).

These and similar properties are called **physical properties**. We often describe and distinguish substances by their conspicuous physical properties, especially the conspicuous or specific properties. For example, (1) copper is a metal, which is an excellent conductor of electricity; (2) water is a colorless, tasteless liquid, which dissolves a great many substances and boils and freezes at definite temperatures.

7. Chemical properties. — In chemistry we study constantly another kind of properties called **chemical properties**. These are the characteristics of a substance exhibited in chemical changes. For example, iron rusts in moist air. That is, the lustrous, hard, metallic solid becomes a rusty brown, porous solid, unlike iron in appearance. Experiments show that iron rust is a different substance from iron. This transformation of iron into iron rust is an example of a **chemical change**. Iron also undergoes a chemical change when treated with other substances besides moist air, *e.g.*, hydrochloric acid and bromine. If we prepared a list of the items, so to speak, in the chemical conduct of iron, these items would make up its chemical properties.

Every substance has a set of chemical properties, which becomes evident when the substance undergoes a chemical change, *i.e.*, a change into one or more new substances. Hence chemical properties are indispensable in recognizing and describing substances.

8. More about properties. — Let us illustrate the meaning of physical and chemical properties by studying sulfur.

(1) Physical properties. Examination shows certain physical properties. (a) It is a yellow, crystalline solid without odor or taste. (b) It is heavier than water, because it sinks when placed in a vessel of water. (c) It is insoluble in water but soluble in another liquid called carbon disulfide. (d) When heated, sulfur melts into a pale yellow liquid, which turns brown at a moderate temperature and remains

so until the temperature is quite high; then it becomes viscous like tar and finally boils, yielding a yellow smoke which looks much like sulfur. (e) Sulfur does not conduct electricity, for when introduced into the circuit of an electric bell, it prevents the ringing of the bell. (f) When rubbed briskly with a piece of silk, sulfur becomes electrified and attracts tiny pieces of paper.

(2) Chemical properties. (a) If sulfur is heated to a high temperature, it takes fire and burns. The flame is blue, and an invisible, suffocating gas is detected by the odor; if burned long enough, all the sulfur is transformed into this gas. (b) If sulfur and a powdered metal, such as iron or copper, are mixed and heated in a test tube, the mixture begins to glow, and the incandescence often spreads throughout the mass even after the test tube has been removed from the flame. The product is neither sulfur nor iron, but another substance which has properties entirely different from those of the original sulfur and metal.

Thus, step by step, we have established by observation and experiment the properties that serve to identify sulfur and to distinguish it from other substances.

9. Chemical change. — Chemistry deals not only with substances and properties, but especially with the chemical

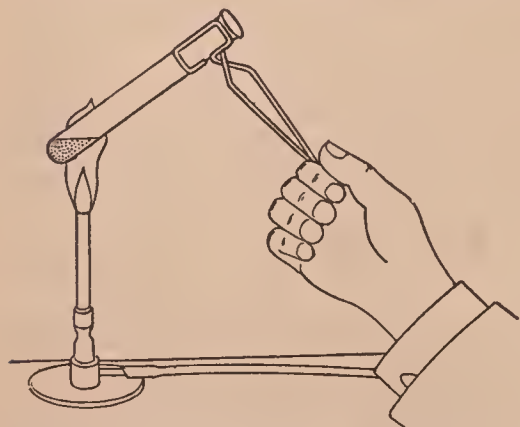


FIG. 3. — Heating a mixture of iron and sulfur in a test tube.

changes which substances undergo or may be made to undergo. Let us consider a simple experiment. Sulfur and iron can be readily distinguished by their properties. Sulfur is a yellow, brittle solid, whereas iron is a gray, silvery solid which is attracted by a magnet. If we pulverize the two substances, mix, and heat in a test tube (Fig. 3), the contents

of the test tube glows, even after removal from the flame. Now if we break the tube and examine the contents, we find it is a hard, black, brittle solid, which has none of the properties of either sulfur or iron. In other words sulfur and

iron have disappeared, so to speak, and a new substance has been formed. This change is an example of a **chemical change**. That is, a chemical change is one which involves the formation of a new substance. Some chemical changes are complex, but all chemical changes have this essential feature, *viz.*, the formation of one or more new (*i.e.*, different) substances.

EXERCISES

1. State characteristic properties of (a) glass, (b) gasoline, (c) water, (d) paper, (e) air, (f) lead, (g) soap, (h) sugar.
2. Define the term *substance* as used in chemistry.
3. Give three examples of chemical change you have observed, tried, or experienced (a) in a kitchen, (b) in a garage, (c) at a fire.

PROBLEMS

(See The metric system, § 328)

1. What is the abbreviation of gram, centigram, liter, meter, cubic centimeter, decimeter, milligram, millimeter?
2. Express (a) 1 liter in cubic centimeters, (b) 2 l. in cc., (c) 1 meter in centimeters, (d) 250 cm. in dm., (e) 1 kg. in grams, (f) 250 gm. in mg., (g) 56.75 l. in cc., (h) 1250 cc. in l., (i) 1 cc. in cu. m.
3. How many cc. in (a) 1 liter, (b) 1 cu. dm., (c) 1 cu. m.?
4. If 1 m. of magnesium ribbon weighs 4 dg., how many mg. will 5 cm. weigh?
5. Into how many pieces 5 cm. long can a glass tube 1 m. long be cut?
6. A flask holds 750 cc. Express its capacity in (a) l., (b) cu. dm.

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

Exercise 1 — Properties and Chemical Change.

SUPPLEMENTARY SECTIONS FROM PART II

326. A good example of chemical change.
328. The metric system (begun).

CHAPTER III

ELEMENTS — COMPOUNDS — MIXTURES

10. Compounds and elements. — In chemistry we deal largely with compounds and elements.

If we heat strongly a little red powder, called mercuric oxide, in a test tube, the powder turns dark, and minute, silvery drops collect on the upper part of the test tube. Now, if we push well down into the test tube a small glowing wooden splint (or a glowing joss stick), the glow increases and the end of the stick bursts into a flame. Clearly a colorless gas, which differs from ordinary air, must have been produced inside the tube.

The two new substances formed from the mercuric oxide are the liquid, mercury, which can be seen, and the colorless gas, oxygen, which mingles with the air (in the test tube). Both substances are quite different from the original red solid, mercuric oxide. Therefore, we have decomposed the mercuric oxide into two different substances, mercury and oxygen — different from each other and from mercuric oxide. Moreover, these new substances, mercury and oxygen, differ from mercuric oxide in a fundamental way, *viz.*, they themselves can not be decomposed by heating or by any other process ordinarily used by chemists — not easily shown in the laboratory, but nevertheless true.

The essential difference, then, between the mercury and oxygen on the one hand and the mercuric oxide on the other is clear. Mercury and oxygen are the fundamental constituents of mercuric oxide. We can decompose mercuric oxide into its constituents, but there the decomposition stops. We have reached the end, chemically speaking. These two

substances, mercury and oxygen, are examples of **elements**. Whereas mercuric oxide is an example of **compounds**.

Obviously mercuric oxide is a compound of the elements mercury and oxygen. Hence, we may say : —

A **compound** is a substance which can be decomposed into two or more fundamental substances called elements, or can be built up from elements.

An **element** is a substance which we have not been able to decompose into simpler substances (§§ 13, 16).

Compounds and elements may be defined in another way. Elements are composed of minute particles called atoms; the atoms of the same element are alike. Compounds are composed of atoms of different elements. Hence we may say : —

An **element** is a substance which consists of the same kind of atoms.

A **compound** is a substance which consists of different kinds of atoms.

In a few words, atoms are fundamental chemical units. Atoms unite to form **molecules**. If the uniting atoms are alike, molecules of an element are formed, *e.g.*, oxygen gas consists of molecules each containing two atoms. If the uniting atoms are different, molecules of a compound are formed, *e.g.*, two atoms of hydrogen and one atom of oxygen form one molecule of water.

11. Characteristics of compounds. — Compounds have several essential characteristics.

(1) The elements in compounds are chemically united. That is, the elements in a compound are not merely mingled or just lying side by side. Only by a chemical change can we decompose a compound into its elements or unite elements into a compound.

(2) The properties of compounds differ from the properties of the elements that compose them. Thus, the blue solid copper sulfate is composed of three elements — the red metal copper, the yellow solid sulfur, and the colorless gas oxygen.

(3) The most important characteristic of chemical compounds is their constant composition. This means that any

given chemical compound always consists of an unvarying per cent of the same elements. For example, the compound water always contains 88.82 per cent of the element oxygen and 11.18 per cent of the element hydrogen. This is a general fact in chemistry and it is so important that it is stated as the **law of constant composition** : —

A chemical compound has a constant composition by weight.

The number of compounds is very large — many thousands. Yet all consist of two or more elements chemically united — each compound having its elements in a certain, fixed proportion, which is characteristic of the compound.

12. Mixtures and compounds. — Not all the materials used or studied in chemistry are elements or compounds. Certain materials contain two or more substances, which can be recognized by the eye (or a magnifying glass), and separated by sifting, dissolving, or filtering. Any material which consists of substances merely mixed or stuck together is called a **mixture**. Many familiar materials are mixtures, *e.g.*, paint, milk, and granite.

Mixtures have certain unmistakable characteristics by which they can be distinguished from compounds.

(1) The ingredients of a mixture may vary in kind and proportion. Thus, soil may be largely sand, or clay, or organic matter, together with many other substances. Indeed, the kind and proportion of ingredients may vary widely and the mixture still have the same name. But in a compound the constituents are chemically united in a fixed proportion.

(2) The ingredients can be readily separated. For example, the starch in flour can be separated from the other parts of the ground kernel by washing out the flour with water. But the constituents of a chemical compound can be separated only by some chemical process.

(3) The properties of a mixture vary with the kind and proportion of the ingredients. But every specimen of a compound has the same properties. For example, a mixture of iron and sulfur may consist of any proportion of the ingredients, and the properties of the mixture will depend

on the proportion; whereas the compound iron sulfide is always alike throughout.

We define a **mixture** as a substance with varying properties and a variable composition. Whereas a compound is a substance with fixed properties and a fixed composition.

13. More about elements. — We shall learn much about elements during our study of chemistry. At present we need know only a few characteristics.

(1) In the chemical changes which are shown by the usual chemical properties, elements are not decomposed. The compound water, for example, can be decomposed into the elements hydrogen and oxygen. But neither hydrogen nor oxygen has been decomposed further into other substances. We can say, therefore, that one marked characteristic of elements is that they are undecomposable substances as far as the usual chemical changes are concerned.

(2) It has been customary for many years to classify as elements those substances which have not been decomposed into simpler substances. It would follow that the elements are the primary forms of matter, so to speak, and are chiefly characterized by stability. This is true of many elements. But this stability we observe in most chemical changes does not necessarily mean that elements are stable under *all* conditions. It is a fact that the rare element radium is spontaneously decomposing into other elements, one of which is helium. Other elements behave similarly. So chemists have been led to give elements another characteristic, *viz.*, a complex structure which makes some of them unstable. Later we shall study radium, which is one of these unstable elements (see §§ 523–536). For the present it will be satisfactory to regard the chemical elements as the fundamental substances from which compounds are formed and into which compounds can be finally decomposed.

There are about ninety elements. Only a dozen are abundant. It is a fact that a few elements by their various combinations furnish most of the substances studied in this book.

We must not forget that the word element is used in two senses. It means, first, a simple substance in the free or un-

combined state, *e.g.*, iron or sulfur. It also means one of the special kinds of matter in a compound, *e.g.*, iron sulfide contains the elements iron and sulfur in the combined state.

14. Each element has a symbol. — Each element is designated by a symbol which is an abbreviation of its name. The symbol is usually the initial letter, or the initial and an appropriate letter of the name of the element. Thus, O is the symbol of oxygen, C of carbon, H of hydrogen, and Zn of zinc. If initial letters are alike, another letter is added, *e.g.*, C for carbon, Ca for calcium, Cl for chlorine. In some cases the symbol is an abbreviation of a foreign name. Thus, Fe is the symbol of iron (*ferrum*), Cu of copper (*cuprum*), Hg of mercury (*hydrargyrum*), Ag of silver (*argentum*), Sn of tin (*stannum*), Pb of lead (*plumbum*), Na of sodium (*natrium*), and K of potassium (*kalium*).

Symbols are used constantly, (1) to designate elements, (2) to represent 1 atom, and (3) to express the relations of elements and compounds in chemical changes. A complete list of the elements and their symbols will be found in the Table on the back inside cover of this book. Important elements and their symbols are shown in Table I.

TABLE I — IMPORTANT ELEMENTS AND THEIR SYMBOLS

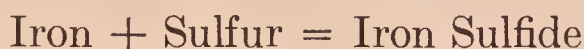
ELEMENT	SYMBOL	ELEMENT	SYMBOL	ELEMENT	SYMBOL
Aluminum	Al	Hydrogen	H	Phosphorus	P
Bromine	Br	Iodine	I	Potassium	K
Calcium	Ca	Iron	Fe	Silicon	Si
Carbon	C	Lead	Pb	Silver	Ag
Chlorine	Cl	Magnesium	Mg	Sodium	Na
Copper	Cu	Mercury	Hg	Sulfur	S
Fluorine	F	Nitrogen	N	Tin	Sn
Gold	Au	Oxygen	O	Zinc	Zn

15. Formulas. — Just as each element is designated by a symbol, so each compound is represented by a formula. A **formula** is a group of symbols — the kind and number of symbols of the elements in the compound. Thus, FeS is

the formula of the compound iron sulfide and H_2O of water. Each formula represents 1 molecule.

16. Interpretation of chemical change by elements and compounds. — In a chemical change (1) elements unite to form a compound, or (2) a compound decomposes into elements; in some chemical changes (3) compounds unite to form other compounds or (4) decompose into other compounds. For example, (1) the element sulfur (S) and the element iron (Fe) unite to form the compound iron sulfide (FeS), (2) the compound mercuric oxide (HgO) decomposes into the elements mercury (Hg) and oxygen (O), (3) the compounds ammonia (NH_3) and hydrogen chloride (HCl) unite to form the compound ammonium chloride (NH_4Cl), and (4) the compound calcium carbonate (CaCO_3) decomposes into the compounds lime (CaO) and carbon dioxide (CO_2).

17. Reactions and equations. — Chemical change is sometimes called chemical action. And a single chemical change is called a **reaction** or an **interaction**. A reaction may be represented by a **chemical equation**, thus: —



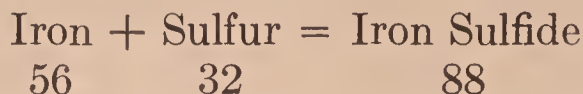
In these simple equations, the plus sign may be read *and* and the equality sign *form(s)*. Thus, briefly, iron and sulfur form iron sulfide. Or, more fully, the elements iron and sulfur when heated together undergo a chemical change which results in the formation of the compound iron sulfide.

In a chemical change there is no loss or gain in the total weight, that is, the elements and compounds merely rearrange themselves in another way. They are not destroyed. Sometimes this general fact is stated in a brief form called the **law of the conservation of matter**, thus: —

In a chemical change substances are not destroyed but merely rearranged in a different way, and hence the final weight is the same as the original weight.

We can represent this fundamental fact by an equation. Thus, 56 parts by weight of iron always unite with 32 parts

by weight of sulfur and form 88 parts by weight of iron sulfide, and the equation is : —

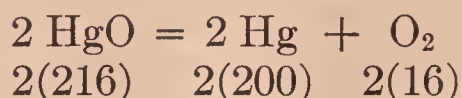


This equation is read: 56 parts of iron and 32 parts of sulfur form (or equal) 88 parts of iron sulfide. By “ parts by weight ” we mean any denomination, *e.g.*, grams, kilograms, pounds, tons.

We usually use symbols and formulas in equations. Thus, the above equation is written : —



This is the correct equation, because Fe stands for 56 parts of iron and S for 32 parts of sulfur. Similarly, for the decomposition of mercuric oxide we write : —



18. Weighing and measuring in chemistry. — In chemistry we do not use the English System of weights and measures. A different system called the Metric System is used. An account of the Metric System is given in § 328. The units of length, weight, and volume should be learned ; also the names, abbreviations, and relations of the denominations in each division, especially weight and volume.

19. Review and summary of Chapters II and III. — The special kinds of materials studied in chemistry are called **substances**. Each substance has its own set of characteristics, called **properties**, by which it is recognized. **Physical properties** include the characteristics readily observed under the usual external conditions. Whereas **chemical properties** include the characteristics revealed when substances undergo fundamental alteration called **chemical changes** — changes in which substances are transformed into other substances. **Elements** are simple substances in the sense that each is one kind of fundamental material which has not been changed by the usual chemical processes into any other kind of simple material. There are about ninety elements. Each element

is designated by an abbreviation called a **symbol**; a symbol represents 1 atom. **Compounds** consist of two or more elements in chemical combination. There are thousands of compounds, and each has a **constant composition**, which is expressed by a **formula**; a formula represents 1 molecule. In **mixtures**, which are often studied, the proportions of the ingredients are not constant, and the properties vary. In **chemical changes** there is no loss or gain in the total weight of the reacting substances. A chemical change, or **reaction**, is expressed by symbols and formulas in a condensed form called an **equation**.

EXERCISES

1. What is an element? A compound? In what fundamental way do elements and compounds differ? Could you prepare (a) a compound from elements, (b) elements from a compound, (c) compounds from compounds, (d) elements from elements?
2. State and illustrate two characteristics of a chemical compound.
3. What are some characteristics of a mixture?
4. (a) How can water be distinguished from gasoline? (b) Copper from iron? (c) Glass from sand? (d) Sugar from starch?
5. Name eight important elements and give the symbol of each.
6. What is the formula of iron sulfide, water, mercuric oxide, carbon dioxide?
7. What is a reaction? An equation? Give an example of each.
8. Interpret this equation by using the terms *compound* and *element*:
Mercuric Oxide = Mercury + Oxygen.
9. State and illustrate the law of constant composition.

PROBLEMS

1. Suppose exactly 3.5 gm. of iron and 2 gm. of sulfur are heated until the chemical change is complete. What weight of iron sulfide is produced? (*Suggestion.* See § 17.)
2. Suppose 5 gm. of iron and 2 gm. of sulfur are heated until the chemical change is complete. (a) What weight of iron sulfide is produced? (b) Is any sulfur or iron left over? (c) If so, which, and how much?
3. What per cent of iron sulfide is sulfur? Iron?
4. When mercuric oxide is made, 25 parts by weight of mercury and 2 of oxygen unite. What is the per cent of (a) mercury and (b) oxygen in mercuric oxide?
5. How many grams of (a) hydrogen and (b) oxygen can be obtained from 150 gm. of water? (*Suggestion.* See § 11.)

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

Exercise *2 — Mixture and Compound.

Exercise S1 — Decomposition of Mercuric Oxide.

(See also Exercises in Weighing and Measuring, end of § 328.)

SUPPLEMENTARY SECTIONS FROM PART II

325. Distribution of the elements.

326. A good example of chemical change (review).

327. Energy and chemical change.

328. The metric system (concluded).

CHAPTER IV

OXYGEN

20. Oxygen is an important element. — Oxygen is first in importance among the chemical elements. Free oxygen is essential to all animal life — without oxygen we would die. It is also necessary in burning fuels.

21. Oxygen is the most abundant chemical element. — Oxygen occurs both free and combined. Free oxygen forms nearly 21 per cent (by volume) of the air. Combined oxygen constitutes 88.82 per cent (by weight) of water, about 50 per cent (by weight) of such common rocks and minerals as granite, limestone, sandstone, clay, and sand. The human body contains about 65 per cent of combined oxygen, while vegetable matter contains about 40 per cent.

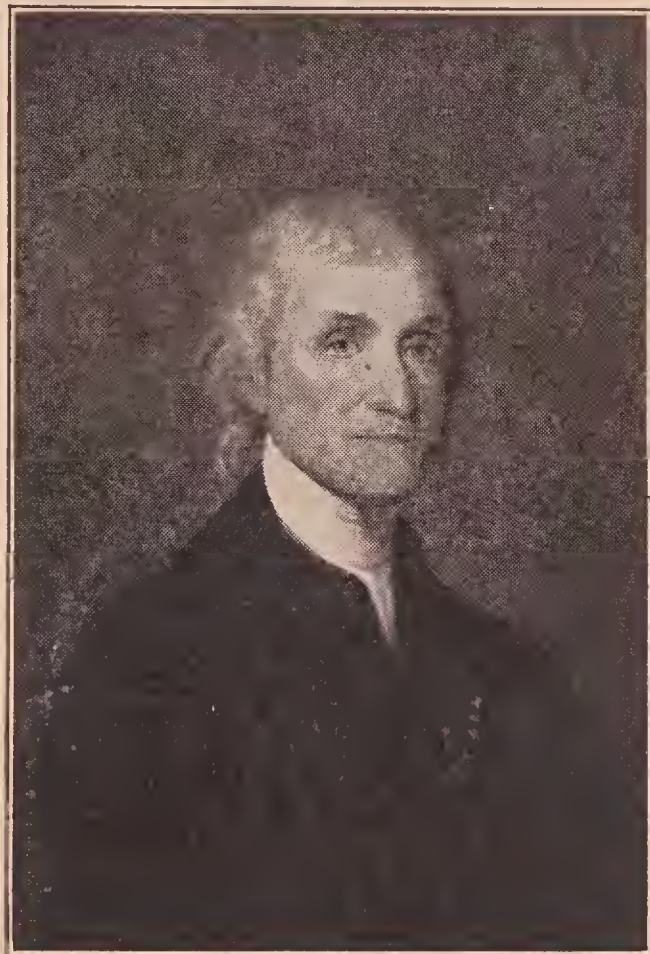


FIG. 4. — The English chemist Priestley (1733–1804), who was one of the first to prepare and study oxygen (1774).

22. Preparation of oxygen. — One of the first chemists to prepare and study oxygen was the English chemist Priestley (Fig. 4). He heated mercuric oxide in a glass vial

and collected the gas in a vessel over water, in much the same way as we do to-day.

Oxygen is more easily prepared from other oxygen compounds, *e.g.*, water and potassium chlorate.

In preparing oxygen from water (H_2O), an electric current is passed through water to which sulfuric acid or sodium hydroxide has been added. Two gases, oxygen and hydrogen, are liberated in separate tubes or compartments. This method is used to prepare oxygen (and hydrogen) on a large scale (Fig. 5).

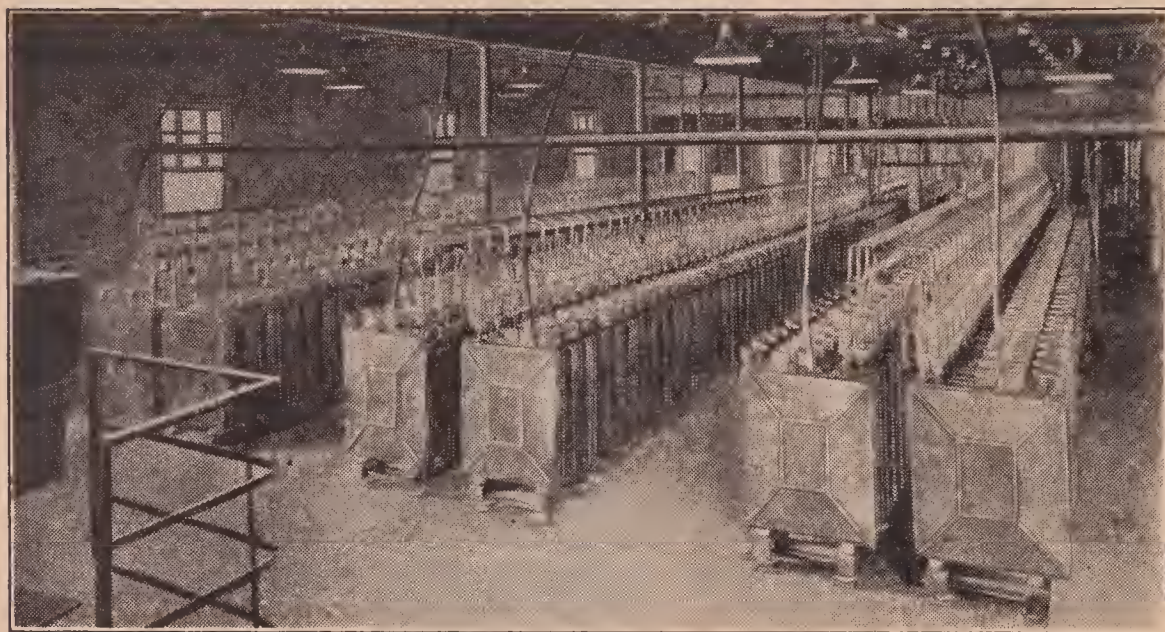


FIG. 5. — A plant for manufacturing oxygen (and hydrogen) by passing an electric current through water containing sodium hydroxide.

Oxygen is most conveniently prepared in the laboratory by heating a mixture of potassium chlorate and manganese dioxide.

The mixture is put in the test tube *A* (Fig. 6), and gently heated. The oxygen escapes through the delivery tube *D* into bottles previously filled with water and inverted over the end of the tube in the pneumatic trough. The oxygen bubbles up into the bottle and displaces the water.

Oxygen is liberated more regularly and at a lower temperature from a mixture of potassium chlorate and manganese dioxide than from potassium chlorate alone. Moreover, after the experiment, all the manganese dioxide can

be recovered unchanged. A substance which affects the speed of a reaction without being ultimately affected itself is called a **catalyst**, and the process is called **catalysis** (compare §§ 31, 193, 224).

Oxygen can be extracted from air. Air is changed into a liquid by great pressure and low temperature. Liquid air is a mixture of liquid oxygen and liquid nitrogen. By allowing liquid air to evaporate at the ordinary pressure, the nitrogen, which is the more volatile of the two liquids, escapes more rapidly than the oxygen. By regulating the evaporation the nitrogen is separated from the oxygen. The gas is compressed into steel cylinders (see Fig. 11).

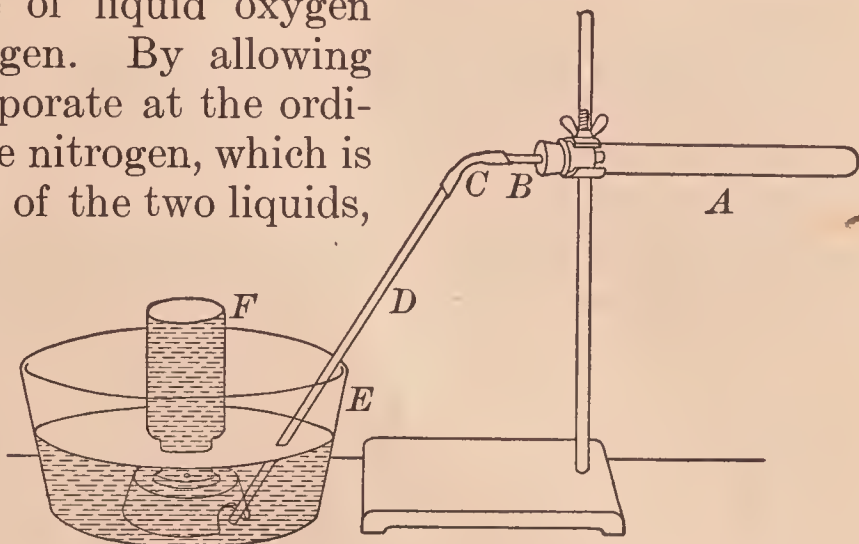
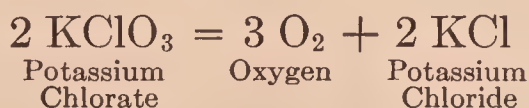


FIG. 6. — Apparatus for preparing oxygen in the laboratory.

23. The preparation of oxygen illustrates one kind of chemical change. — Potassium chlorate decomposes into oxygen and potassium chloride. This chemical change may be expressed by the equation: —



This kind of chemical change is called **decomposition**, that is, a chemical change in which a compound is broken up chemically into other elements, compounds, or both.

24. Physical properties of oxygen. — Pure oxygen is colorless, odorless, and tasteless. (Certain impurities may give a slight odor and taste to the gas as prepared in the laboratory.) It is not very soluble in water — only 3 cc. dissolve in 100 cc. of water at the ordinary temperature. For this reason it can be readily collected and stored over water.

Oxygen is slightly heavier than air. One liter weighs 1.43 grams, if measured and weighed at the temperature of

0° C. and 760 mm. (*i.e.*, zero degrees as registered by a centigrade thermometer and pressure of 760 millimeters as registered by a barometer).

25. Chemical properties of oxygen. — Oxygen unites with many elements and interacts with many compounds. This combining is often accompanied by light and heat (Fig. 7).

At ordinary temperatures oxygen unites slowly with several elements, *e.g.*, lead and copper. We describe this change by saying these metals tarnish or rust, *i.e.*, they combine slowly with the oxygen of the air.

At higher temperatures the chemical conduct of oxygen is conspicuous. Thus, a faintly glowing piece of charcoal

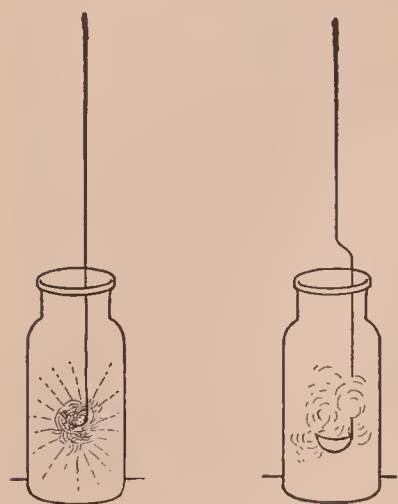


FIG. 7. — Sulfur (right) and iron (left) burning in a bottle of oxygen.

when put into a bottle of oxygen bursts immediately into flame. Sulfur burns in air with a feeble bluish flame, but in oxygen the flame becomes large and brilliant (Fig. 7). Iron can hardly be made to burn in air, but if steel wool (matted strands of iron) is merely heated and thrust into a bottle of oxygen, the iron burns, sends off a shower of sparks, and often forms drops of molten iron (Fig. 7).

Oxygen also reacts with many compounds, especially compounds like those in wood, paper, gasoline, fuel oil, and numberless compounds associated with plants and animals (§§231, 253). The chemical action with compounds, as a rule, is not direct combination with the compound itself as in the case of elements, but with the carbon and hydrogen freed by the decomposition of the compound (§ 29).

In such experiments as just described, the oxygen itself does not burn. It assists the burning of the other elements. So if we were to describe briefly the chemical conduct of oxygen, we should say oxygen does not burn but assists the burning of other substances. The conspicuous chemical conduct of oxygen — not burning but assisting burning — is sometimes called its chief chemical property.

26. Test for oxygen. — An experiment by which we try to identify an element or a compound is called **testing or making a test**. The decisive behavior of a substance under stated conditions is called the **test** for the substance. Thus, the test for oxygen is its chief chemical property, *viz.*, the gas does not burn, but assists the burning of a glowing splint.

27. The chief chemical property of oxygen illustrates chemical change. — A chemical change like that taking place between oxygen and sulfur is the combining of oxygen and sulfur. The product is a compound of the two elements. This kind of chemical change is called **combination**, that is, a chemical change in which compounds are formed by the chemical union of two or more substances.

28. Oxidation and oxides. — The chemical change in which oxygen unites with a substance is called **oxidation**. The substance which unites with the oxygen is said to **undergo oxidation**. Substances which furnish the oxygen are **oxidizing agents**. Free oxygen and air are oxidizing agents, though the oxygen for oxidation is often provided by certain compounds of oxygen, such as potassium chlorate (KClO_3), nitric acid (HNO_3), lead dioxide (PbO_2), and potassium permanganate (KMnO_4). The compound formed by the union of oxygen and another element is called an **oxide** of the element.

Oxides of different elements are distinguished by placing the name of the element (or a slight modification of it) before the word oxide, *e.g.*, magnesium oxide, nitric oxide. Sometimes di-, or a similar numerical syllable, is prefixed to the word oxide, *e.g.*, manganese dioxide (MnO_2), sulfur trioxide (SO_3), phosphorus pentoxide (P_2O_5).

29. Oxidation of compounds. — Oxidation is by no means limited to elements. Many compounds burn readily, *i.e.*, combine as a whole with oxygen. Thus, carbon monoxide (CO) unites directly with oxygen to form carbon dioxide (CO_2). Sometimes the compound decomposes and the parts then unite with oxygen. Thus, the ingredients of gasoline are compounds of hydrogen and carbon, called hydrocarbons (§ 246). When gasoline burns, the hydro-

carbons decompose, the hydrogen burning to water (vapor) and the carbon to carbon dioxide.

30. Combustion is oxidation. — During oxidation heat is liberated, and if the heat is intense, light is also produced.

Different substances react with oxygen, *i.e.*, oxidize, at different rates. If oxidation is slow, as in the rusting of some metals, the temperature does not change appreciably, and the heat escapes about as fast as it is produced (Fig. 8). If oxidation is rapid, heat is liberated quickly, the temperature rises suddenly, and the substance burns, often with dazzling light. Rapid oxidation which produces heat and light is called **combustion** (Fig. 9). In ordinary language combustion means fire or burning; in chemical language it means rapid oxidation.

Combustible substances are those which burn, *e.g.*, wood, petroleum, coal. Whereas incombustible substances are those which do not burn, *e.g.*, brick, glass, stone, cement, asbestos — all “fire proof” material.

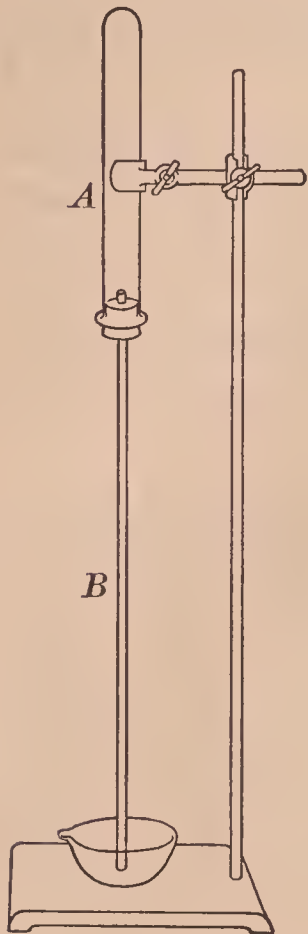


FIG. 8. — Apparatus to show slow oxidation. The test tube A is moistened and iron in the form of filings or thread is put inside. The lower end of B rests in the vessel which is full of water. As the iron is slowly oxidized, water rises in B and partly fills the test tube.

31. The rate of oxidation. — This depends on several factors. An important one is temperature. Most combustible substances do not burn at all at ordinary temperatures, but do so rapidly if the temperature is raised.

Another factor is the form or shape of the substance. Shavings burn faster than kindling wood, and the kindling wood in turn faster than a log. Similarly, powdered coal is used in cement kilns where lump coal would be useless, and

fuel oil is sprayed into a furnace instead of being dropped in.

Still another factor is availability of oxygen. To make a fire burn we increase the supply of oxygen by opening the

draft, and to shut it down, we lessen the supply by closing the draft. A log once on fire burns rapidly if the wind blows upon it. In extracting iron from iron ore, and in one process of making steel, air is blown through the hot mixture.

A useful factor is **catalysis**, *i.e.*, the process of hastening a reaction by some substance which apparently does not enter into the chemical change (§§ 22, 78, 193, 224). Thus, in making sulfuric acid, sulfur dioxide is passed over platinum to hasten the oxidation of the dioxide to sulfur trioxide (§ 224).

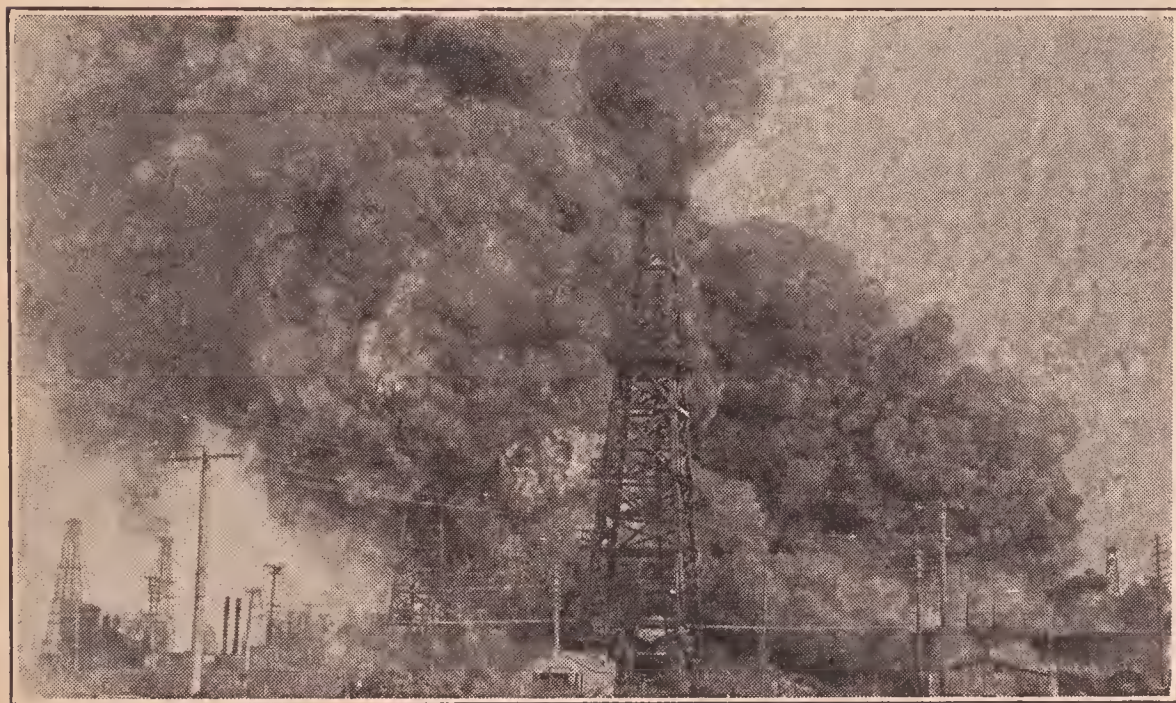


FIG. 9. — Rapid oxidation — a Southern California oil well on fire.

Finally, the rate of oxidation is affected by a factor which might be called unusual local conditions. For example, if the heat liberated during slow oxidation can not escape readily, the temperature will rise steadily to such a point that the substance takes fire. Thus, oily rags carelessly thrown aside by painters or machinists, moist hay stored in a poorly ventilated barn, and soft coal kept in a pile a long time in the air sometimes take fire without apparent cause. Such fires, often unexpected and disastrous, are said to be due to **spontaneous combustion**, though they are simply cases of slow oxidation which becomes accelerated by accumulated heat.

32. Importance of oxidation. — Rapid oxidation is essential to our health, comfort, and progress. We burn wood, gas, oil, and coal to cook our food and heat and light our houses. So also we use these fuels as sources of energy to furnish the power in countless industries by which we prepare materials needed for food, shelter, and clothing.

Slow oxidation is also important. For example, in breathing, air is drawn into our lungs. Here the oxygen forms an easily decomposed compound with the hæmoglobin of the blood, which distributes the oxygen compound to the tissues of the body. And this oxygen slowly oxidizes the digested food and the worn-out tissues of the body. By this slow oxidation, heat is liberated which keeps the body warm and maintains it at the proper temperature (37°C. or 98.6°F.) for life processes.

The decay of organic matter is also due largely to slow oxidation. Water is purified by spraying it into the air where organic matter is slowly oxidized (§ 81). Sewage, too, is often sprayed into the air to hasten the decomposition of substances in the sewage by slowly oxidizing the carbon compounds to carbon dioxide and water.

The hardening of paint is not due to drying in the popular sense but to slow oxidation of the linseed oil in the paint. Driers are added which act as catalysts in hastening the oxidation of the thin layer of oil, which finally makes the color stick to the painted surface.

33. Combustion was first interpreted by Lavoisier. — The answer to the question “What happens when a substance burns?” was delayed many years by a false theory called the **phlogiston theory**. The advocates of this theory believed that “combustible substances contain a principle called phlogiston, and that when a substance burns, phlogiston escapes.” This false theory was held until about 1775 when the French chemist Lavoisier (Fig. 10) proved by his own and others’ experiments: (1) that phlogiston did not exist, and (2) that ordinary combustion is a process of combining with “a certain substance contained in the air.” Soon after, he showed that this “substance” is identical

with the gas discovered by Priestley in 1774. In 1778 Lavoisier named the gas oxygen.

34. Oxygen is essential to life. — Free oxygen is essential to all forms of animal life. As stated in § 32 in breathing, air is drawn into our lungs; here the oxygen of the air is taken up by the blood, which distributes it to all parts of the body, where oxidation occurs. By this slow oxidation, waste products are formed and heat is supplied to the body. Two of these waste products are carbon dioxide and water vapor, which are exhaled from the lungs; water vapor is also given off through the skin.

35. Uses of oxygen.— Oxygen is often administered to persons who are too ill or weak to inhale the ordinary volume of air, *e.g.*, in cases of pneumonia or shock from surgical operations. In submarine boats the oxygen of the air used up is replaced by oxygen released from tanks. Aviators and mountain climbers (*e.g.*, the Mt. Everest parties) are equipped with oxygen tanks and breathing apparatus to supply quickly the oxygen needed at high elevations.

Oxygen is used in mixtures of gases which burn with intense heat. Thus, acetylene (a compound of carbon and hydrogen (C_2H_2), when burned with oxygen in a proper apparatus (called an acetylene torch or blowpipe) produces one of the hottest known flames (about $3000^\circ C.$)).

Ordinary tools cut hard metals slowly, but the tip of the

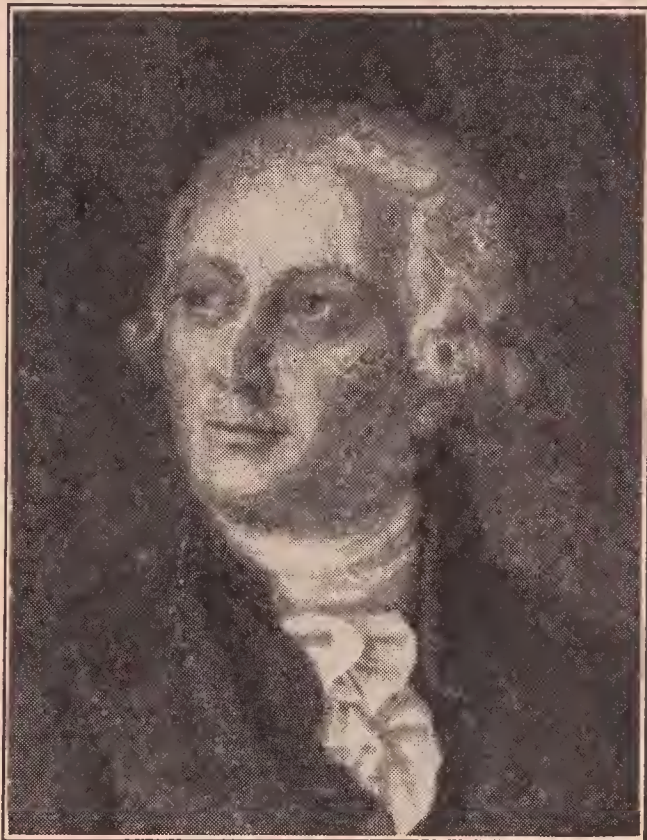


FIG. 10. — The French chemist Lavoisier (1743–1794), who overthrew the false theory of phlogiston, explained combustion correctly, and laid the foundations of modern chemistry.

oxy-acetylene flame when passed slowly across the metal melts ("cuts") it very quickly. Metal structures, such as fences, bridges, frames of buildings, "scrapped" warships, etc., are speedily dismantled by this flame. The fire department of large cities is equipped with an oxy-acetylene outfit for cutting a passage through steel doors of vaults or effecting an entrance into parts of a fireproof building.

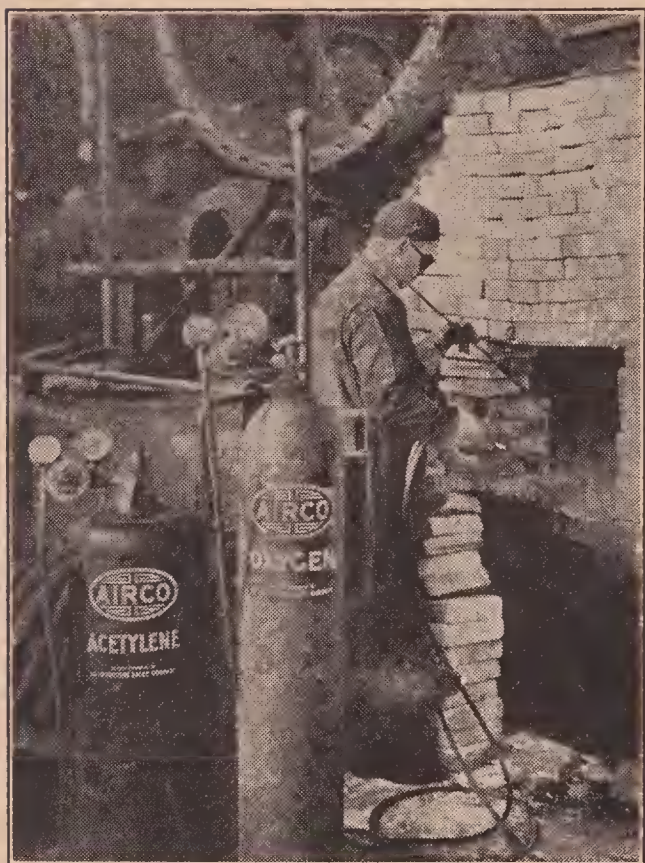


FIG. 11. — Welding with an acetylene torch. A cracked cylinder of a locomotive is being welded just inside the opening in the temporary brick wall.

The oxy-acetylene flame is used for welding (Fig. 11).

36. Saving lives by oxygen apparatus. —

Oxygen is used in various forms of breathing apparatus for rescue work. The **pulmotor**, or lung-motor, is essentially a pump by which air rich in oxygen can be forced into the lungs at about the same rate as we breathe. The pulmotor is used to resuscitate persons who have been overcome by smoke or poisonous gases (*e.g.*, illuminating gas) or who have been rendered unconscious by drowning or by an electric shock. Fire

departments and police stations are supplied with pulmotors.

Another form of rescue apparatus can be hung from the shoulders like a knapsack. The man's nose is clipped so he must breathe through his mouth (Fig. 12). Flexible tubes connect his mouth with a breathing bag (right), a cylinder of compressed oxygen (gas) and a regenerating can (left); the can contains potassium hydroxide to absorb the water vapor and carbon dioxide exhaled from the lungs.

A man provided with an oxygen-breathing apparatus can

safely enter places where the air contains smoke or poisonous gas, and make repairs, extinguish fires, or rescue workmen who have been overcome. Extensive use is made of this kind of rescue apparatus in mine disasters.

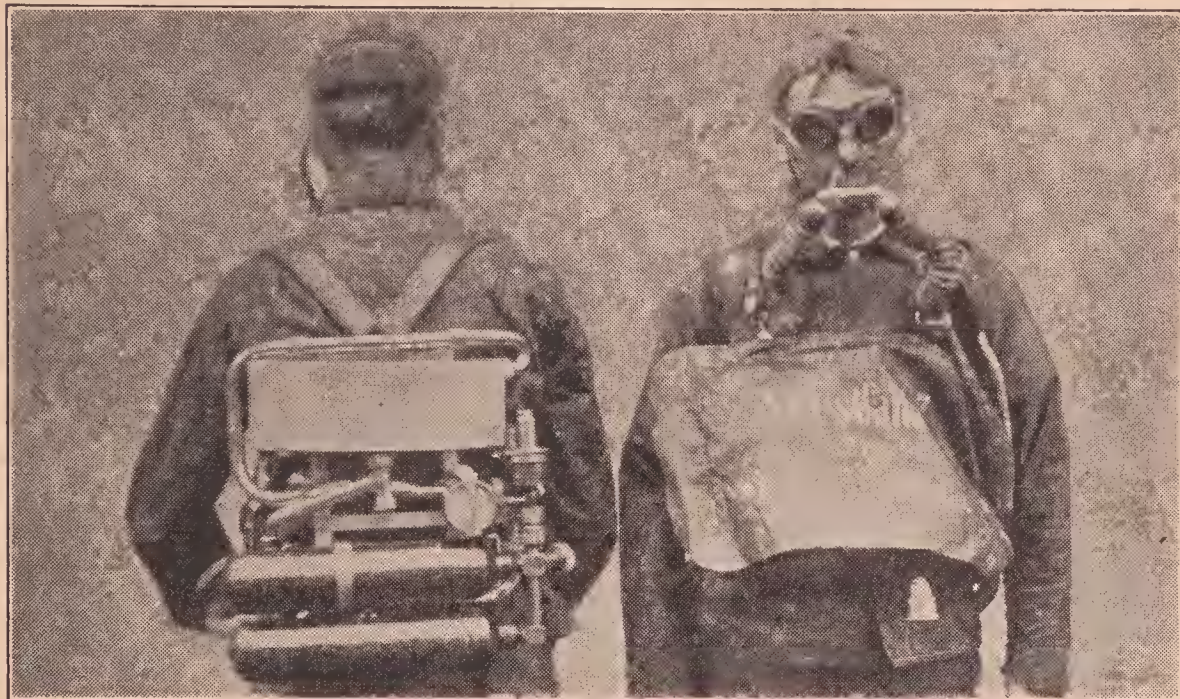


FIG. 12. — Man equipped with oxygen-breathing apparatus. He breathes through his mouth from the gas bag carried on his chest (right). The tank of oxygen and the regenerating can are carried on his back (left).

EXERCISES

1. State three important physical properties of oxygen.
2. Prepare written answers to these questions: (a) Why does a draft of air make a fire burn well? (b) Why does a draft of air sometimes extinguish a candle flame? (c) What oxides are found in the home? (d) How do fish obtain oxygen?
3. (a) Make a list of the name and symbol of each element mentioned in studying oxygen. (b) Make a list of the compounds mentioned in this chapter. (c) Learn the formula of each compound (as given).
4. Define (a) oxidation and (b) oxide. Name five oxides.

PROBLEMS

1. How many gm. of oxygen are in a bottle holding 2.5 l. (at 0°C . and 760 mm.)?
2. (a) How many liters (at 0°C . and 760 mm.) will 25 gm. of oxygen occupy? (b) How many gm. will 25 l. of oxygen weigh?
3. A pupil prepared five bottles of oxygen, each holding 250 cc. (at 0°C . and 760 mm.). How many gm. of oxygen were prepared?

4. Water contains 88.82 per cent of oxygen. If 0.5 kg. was decomposed, how many liters of oxygen (at 0° C. and 760 mm.) were formed?

5. Potassium chlorate contains 39.18 per cent of oxygen. If 35 gm. are decomposed, (a) how many gm. of oxygen are liberated, and (b) how many bottles each containing 250 cc. will the gas fill?

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

Exercise *3 — Preparation and Properties of Oxygen.

Exercise 4 — Heating a Known Weight of a Metal in Air.

Exercise S2 — Examples of Chemical Change in Exercise *3.

Exercise S3 — Preparation of Oxygen (Short Method).

Exercise S4 — Preparation of Copper Oxide. (See Exercises *6, *10, and S10.)

Exercise S5 — Slow and Rapid Oxidation — T.

SUPPLEMENTARY SECTIONS FROM PART II

329. Preparation of oxygen from various substances.

330. Lavoisier's famous experiment.

331. Oxidation and energy.

CHAPTER V

CARBON — CARBON DIOXIDE — CARBON MONOXIDE

37. Carbon is an important and useful element. — Next to oxygen, the most important element is carbon. It is also a useful element. Like oxygen, carbon is found both free and combined in nature. Free carbon is the familiar black solid that makes up the greatest part of hard coal, charcoal, coke, and graphite. And strange as the contrast seems, the highly prized gem called diamond is also free carbon — pure crystallized carbon.

38. Carbon forms a large number of compounds. — The natural and manufactured compounds of carbon number over 200,000. Most of them are called organic compounds, because they are so closely related to living things.

All living things contain carbon compounds, which by their chemical changes sustain life. Many common substances which are products of living things are compounds of carbon with hydrogen and oxygen, *e.g.*, sugar, starch, fat, and cotton, while others consist essentially of substances which are compounds of carbon, hydrogen, oxygen, and also nitrogen, *e.g.*, flour, wool, and meat. Carbon united with hydrogen forms a large class of compounds called **hydrocarbons**, which are the main ingredients of illuminating gas, natural gas, petroleum, kerosene, gasolene, fuel oil, lubricating oils, paraffin wax, and turpentine.

The manufactured compounds of which carbon is the central element include dyes, drugs, medicines, photographic developers, perfumes, soap, ink, and a large number of other substances needed for business and pleasure.

The commonest inorganic compounds of carbon, *i.e.*, those related fundamentally to non-living things, are the carbonates and the oxides. The **carbonates** are compounds of carbon with oxygen and a metal (such as calcium, magnesium or sodium). Thus, calcium carbonate (CaCO_3) is the natural substance limestone, marble, or chalk. Sodium carbonate (Na_2CO_3) is the common substance washing soda; it is manufactured in large quantities. There are two carbon oxides — carbon dioxide (CO_2) and carbon monoxide (CO).

39. Diamond. — The purest natural form of carbon is diamond. As found in mines, principally in South Africa, diamonds are usually rough looking stones, which must be

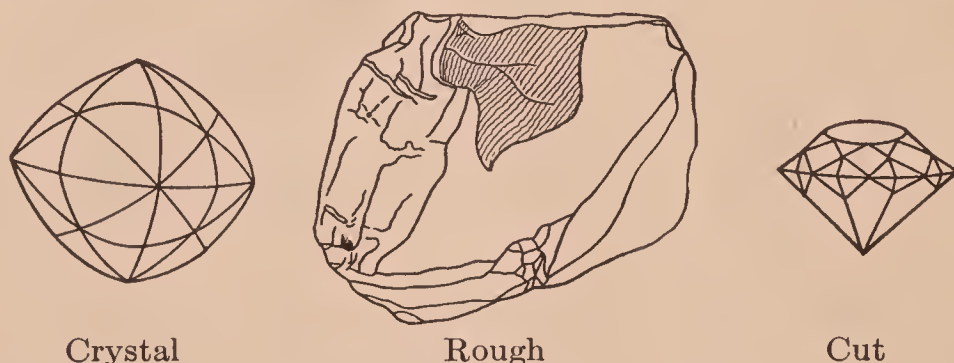


FIG. 13. — Diamonds.

ground, or “cut,” into special shapes and polished to bring out the luster and make them sparkle in the light (Fig. 13).

Diamond is one of the hardest substances known, and can be “cut” and polished only by rubbing with diamond powder, which has very sharp, hard edges.

Diamond resists the action of most chemicals. It combines with oxygen when the two elements are heated together to a high temperature. By this experiment it can be shown that diamond is carbon, for when pure diamond is burned in oxygen, the only product is carbon dioxide.

Diamonds are sold by a weight called a carat; 1 carat = 200 milligrams.

40. Graphite. — Graphite is a dark lead-colored, shiny solid. When rubbed or powdered, it becomes minute, smooth, soft, slippery scales. Hence it leaves a black mark on paper. This property is utilized in the lead pencil.

In making lead pencils, the graphite is washed free from impurities, ground to a fine powder, mixed with clay, and then pressed through perforated plates, from which the "lead" issues in tiny rods. These are dried, cut into the proper lengths, baked to remove all traces of moisture, and then inserted in the wooden case. Varying proportions of clay produce different degrees of hardness.

Pure graphite is carbon ; but it is sometimes called "black lead," or plumbago, because it was formerly supposed to contain lead.

Unlike diamond, graphite is a good conductor of electricity, and for this reason it is often used to coat molds in electrotyping. It resembles diamond in its insolubility in liquids at the ordinary temperature.

Graphite changes into carbon dioxide when heated intensely in oxygen. But it can be heated to a very high temperature in the air without melting or oxidizing. Because of its infusibility it is sometimes used to make stove polish, protective paints, and the electrodes of electrical apparatus in which great heat is produced. It is the principal ingredient of the mixture (graphite and clay) which is made into graphite crucibles ; these crucibles can be heated to a high temperature without melting or oxidizing, and certain metals, *e.g.*, crucible steel, are made in them.

Graphite, owing to its slipperiness, is used as a lubricant, particularly where oil might clog, *e.g.*, on the sliding wooden parts of an organ. Some varieties of artificial graphite can be ground into very fine particles. If ground with tannin (or a similar substance), and mixed with oil or water, this graphite remains suspended a long time. Such suspensions, known as oildag or aquadag, make excellent lubricants.

Graphite is not attacked by corrosive chemicals, *e.g.*, chlorine and sodium hydroxide. Hence, manufactured graphite, in the form of rods, plates, and slabs, is an indispensable article in electrochemical industries (§§ 49, 51, 313, 411, 500).

Native graphite occurs most abundantly in Ceylon. **Graphite is manufactured** at Niagara Falls by heating a special grade of hard coal in a limited supply of air in an electric furnace. The process is electrothermal, *i.e.*, the

chemical change is brought about by the intense heat produced by passing an electric current through the materials (Fig. 14). Articles of almost any size and shape can be made of artificial graphite.

41. Amorphous carbon. — This group includes coal, charcoal, lampblack, coke, and gas carbon. They are varieties of impure carbon. The word amorphous means without crystal form; it is often used to designate uncrystallized, or very fine, substances.

42. Coal. — There are many varieties of coal (Fig. 15). **Bituminous coal** (soft coal) contains about 70 per cent of

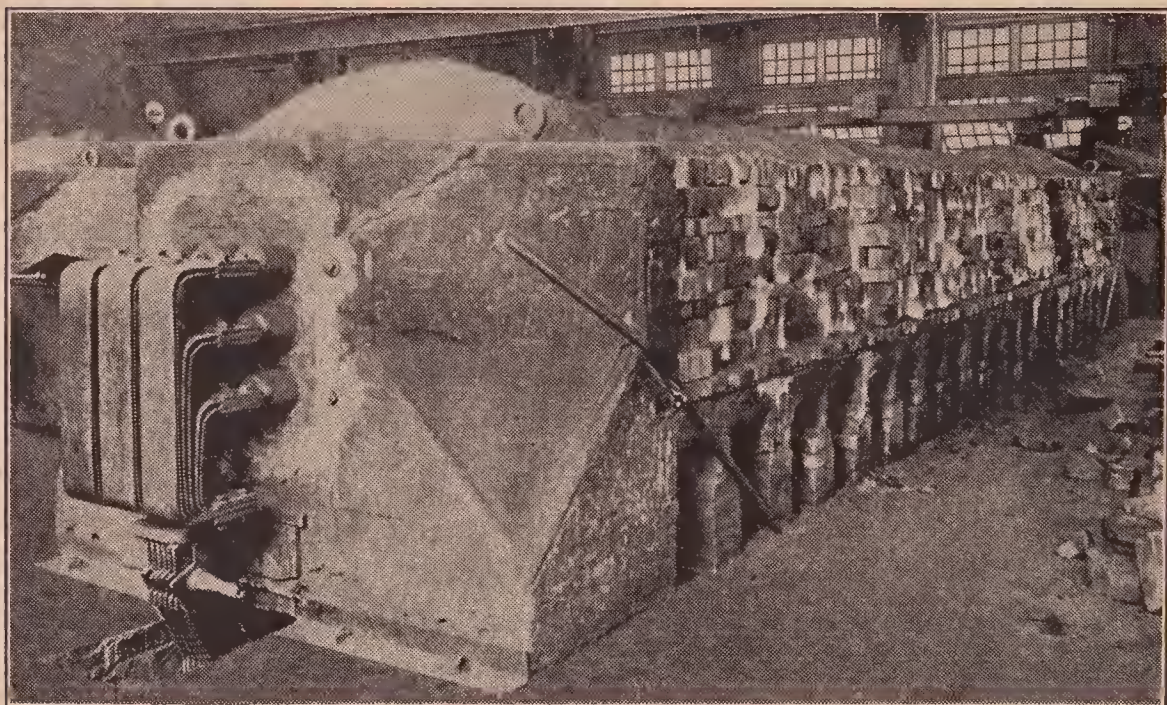


FIG. 14. — An electric furnace for making graphite.

carbon. It burns with a smoky flame and is used as a fuel for steam, and to make illuminating gas and coke. **Anthracite coal** (hard coal) contains 90 per cent or more of carbon. It ignites with difficulty, burns with little or no flame, and produces considerable heat. It is used mainly for domestic purposes — heating and cooking — especially in eastern United States. **Lignite**, or brown coal, contains only a small proportion of carbon, sometimes as low as 20 per cent. It is used as a fuel in some localities, especially near the deposits.

Besides carbon, coal contains moisture and mineral matter; and soft coal, especially, contains considerable volatile matter.

43. Charcoal. — This substance is obtained by heating wood, bones, and other organic matter in closed vessels, or by partially burning them in the air. More or less charcoal may be obtained by heating many organic substances; the charring, as it is called, is one **test for combined carbon**.

Wood charcoal is a black, brittle solid. It burns without flame or much smoke, and leaves a white ash, which consists of mineral substances originally in the wood. It resists



FIG. 15. — Sorting coal in a breaker at a coal mine.

the action of moisture and many chemicals; hence fence posts, telegraph poles, and wooden piles are often charred before being put into the ground.

Most varieties of wood charcoal are very porous and are good absorbers of gases. Charcoal made from fruit stones and cocoanut shells is dense, though porous enough for use in gas masks to adsorb, *i.e.*, take up or absorb, poisonous gases. Charcoal is sometimes used in small household filters to purify drinking water. Charcoal used for such a purpose must be frequently renewed or often heated to redness; otherwise it becomes clogged and contaminated.

Wood charcoal is made by heating wood in closed furnaces, no air whatever being admitted. By this method, which is called **dry distilla-**

tion, the yield of charcoal is about 30 per cent. From the condensed volatile matter acetic acid and methanol (or "wood alcohol") are obtained (§§ 264, 265).

Animal charcoal or boneblack is made by heating bones and animal refuse in a closed vessel. Animal charcoal made from bones contains only about 10 per cent of carbon, which is distributed throughout the porous mineral matter of the bone (largely calcium phosphate). Animal charcoal is used as a pigment, especially in making shoe-blackening. It is also extensively used to remove colored substances from

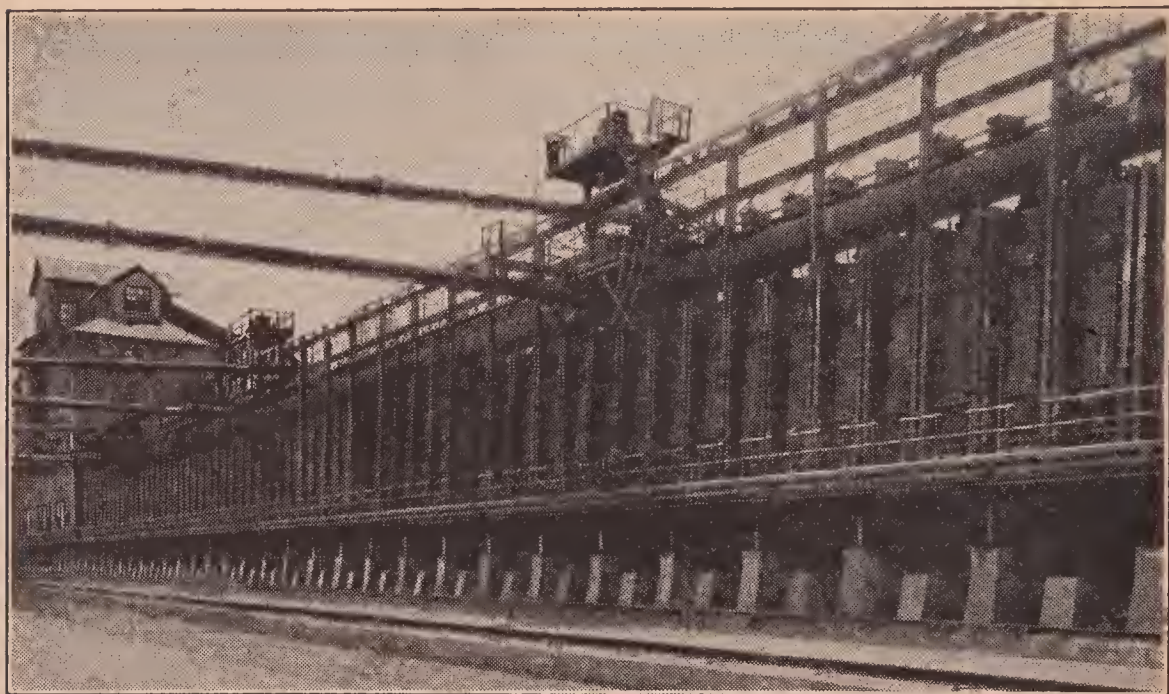


FIG. 16. — A battery of by-product coke ovens at one of the Ford automobile plants.

sugar sirups; the straw colored solution is clarified, *i.e.*, made colorless, by filtering through layers of bone charcoal.

44. Coke. — This variety is made by expelling the volatile matter from bituminous coal, somewhat as charcoal is made from wood. It is left in the retorts when coal is distilled in the manufacture of coal gas (§ 250). On a large scale it is made by heating a special grade of soft coal in huge closed furnaces (Fig. 16), constructed so as to save the by-products, *e.g.*, ammonia, tar, organic compounds, and combustible gases.

Coke is a grayish, porous solid, harder and heavier than charcoal. It burns with no smoke and a feeble flame. Its most extensive use is in the iron industry.

45. Gas carbon. — This is a black, heavy, hard solid, which is deposited inside the retorts in the manufacture of illuminating gas (§ 250). It is almost pure carbon. Being a good conductor of electricity, it is extensively used for the manufacture of the carbon rods of electric lights and for plates of electric batteries.

46. Lampblack. — This form of carbon is prepared by burning gas, oil, or oily substances rich in carbon in a limited supply of air. The dense smoke is finely divided carbon.

Lampblack is one of the purest forms of amorphous carbon. It is used in making printer's ink, black enamel, and certain black paints.

47. Physical properties of carbon. — Many physical properties have been given in the preceding sections.

Carbon does not melt, though it volatilizes at high temperatures, *e.g.*, at the temperature of the electric furnace. It is insoluble in the ordinary solvents. Some molten metals dissolve it, especially iron, which may dissolve as much as 1 per cent of its weight of carbon. As the solution cools some of the carbon separates as crystals of graphite (§ 40) or of diamond (§ 39). Carbon, particularly the very porous forms of charcoal, has the property of adsorption to a marked degree, that is, it takes up or adsorbs large quantities of gases like ammonia and poison gases, and also fine solids like the coloring matter in sirups.

48. Chemical properties of carbon. — Carbon does not interact with acids or bases. At ordinary temperatures carbon is an inert element, *i.e.*, is chemically inactive. But as the temperature is raised, its activity increases until at high temperatures it is very active. Thus, carbon heated with oxygen forms carbon dioxide and carbon monoxide.

At high temperatures carbon withdraws oxygen chemically from oxides. Extensive application of this property is made in extracting metals from ores, *e.g.*, iron from iron oxide (§ 305). The chemical removal of oxygen from oxides (and certain other oxygen compounds) is called **reduction**. The substance bringing about the change is called a **reducing agent**. Thus, carbon is a reducing agent.

49. Carbon disulfide. — This substance (CS_2) is made by direct combination of carbon and sulfur. In Fig. 17, EE are the carbon electrodes. C is charcoal and coke is fed in at KK . Sulfur is fed in at SSS , and accumulates at Z . The carbon disulfide vapor escapes through the pipe P and is condensed in a special apparatus.

Carbon disulfide is a highly combustible liquid (keep it away from flames!). The odor is disagreeable and the vapor is poisonous. It is used as a solvent for rubber, gums, fat, and some forms of sulfur. Large

quantities are used to destroy weevil in grain and in other seeds. It is effective in exterminating ants, mice, moles, and woodchucks, if the holes are closed after the carbon disulfide has been poured in.

50. Calcium carbide. — This substance (CaC_2) is made by heating a mixture of carbon and calcium oxide (CaO) in the electric furnace. With water, calcium carbide forms acetylene (C_2H_2). Acetylene, if burned in a special burner which admits much air, produces a brilliant flame, and is used to illuminate caves and mining camps. With oxygen, acetylene forms a mixture which burns with an intensely hot flame, which is used in welding and "cutting" metals (§ 35).

51. Silicon carbide. — This substance (SiC), better known as **carborundum**, is made by heating silica (silicon dioxide, SiO_2) and coke in the electric furnace. It is an extremely hard substance, nearly as hard as diamond. Its hardness has led to extensive use as an abrasive, *e.g.*, grinding

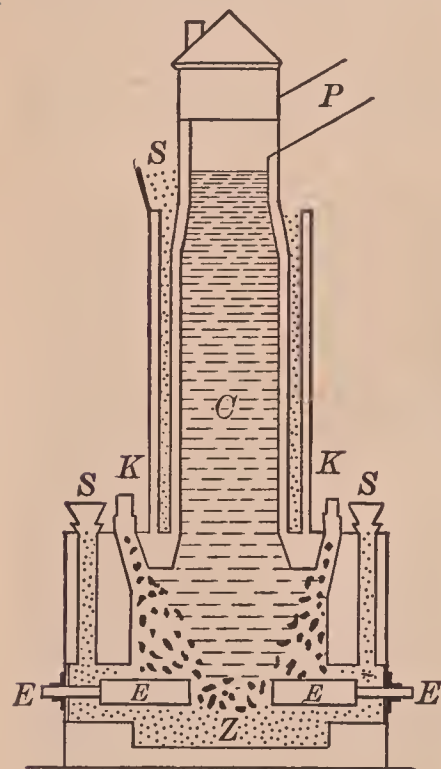


FIG. 17. — Electric furnace for making carbon disulfide from carbon and sulfur.

wheels, cutting stones, polishing cloth, and special shapes used particularly in the automobile industry (Fig. 18).

52. Carbon is an allotropic element. — Carbon exists in three different modifications — diamond, graphite, and amorphous carbon (typified by charcoal prepared from sugar). All pure forms of these different substances are carbon. They can be changed into one another. Indeed, graphite is manufactured from coal (§ 40), diamonds have been made from pure charcoal, and carbon becomes graphite in cast iron (§ 306). Each modification burns in oxygen and yields only carbon dioxide. Furthermore, a given weight of each, say 12 gm., yields the same weight of carbon

dioxide (44 gm.). Why are they so different? Recent experiments show that diamond and graphite have a different structure, or in other words, they are built from the same material but built in a different way.

53. Carbon and energy. — When carbon and certain carbon compounds (*e.g.*, carbon monoxide and hydrocarbons (§ 246)) burn, considerable heat is liberated. This means that the chemical energy stored in the carbon and its compounds is transformed in part into heat energy. Since many forms of carbon and many kinds of carbon com-

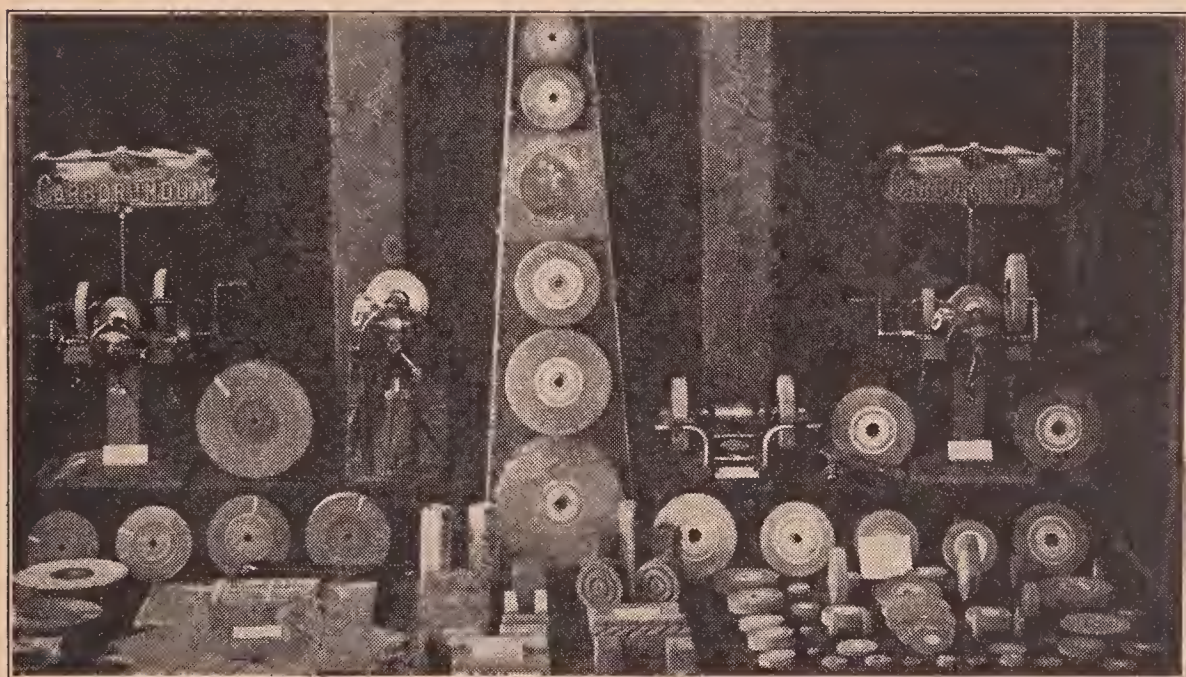


FIG. 18. — Articles made of carborundum.

pounds can be readily obtained, they are extensively used as fuels. (See Chapter XIX.)

Solid fuels are essentially free carbon, though all, especially soft coal, contain other substances, *e.g.*, moisture, volatile substances, and mineral matter (the last is left as ashes after the coal is burned). Liquid fuels are mixtures of hydrocarbons, *i.e.*, compounds of carbon and hydrogen. Gaseous fuels contain hydrocarbons, carbon monoxide, and hydrogen.

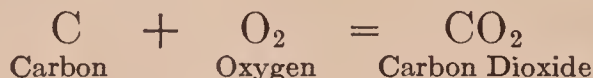
Fuels burn when heated to the proper temperature in a current of air. Chemically this means that the free hydrogen, the carbon and hydrogen from the decomposed compound, and the carbon monoxide combine with oxygen. Physically

this means that heat is liberated. Indeed, the essential characteristic of a good fuel is its heat-producing capacity.

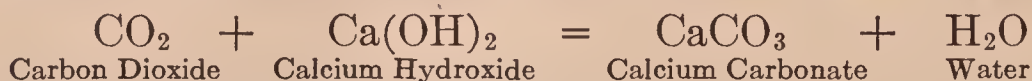
CARBON DIOXIDE

54. Formation of carbon dioxide. — Carbon dioxide is formed when carbon burns in oxygen and also when a candle and other combustible substances burn in air. The process called burning or combustion consists usually in the union of carbon (and also, of course, hydrogen, if present) with oxygen (§ 33). This means that carbon dioxide is being formed constantly by the burning of such common fuels as wood, paper, coke, coal, charcoal, oil, and gas. In fact, carbon dioxide is always one of the **products of combustion**, as they are often called, yielded by burning any substance which contains carbon, *e.g.*, sugar, starch, wax, meat, milk, camphor, alcohol, oil, dyes, fat, and drugs.

The equation for the combustion of carbon is: —



The presence of carbon dioxide in the products of combustion can be shown by bubbling the products, *e.g.*, smoke, through calcium hydroxide solution, or merely by shaking the products with the solution. The calcium hydroxide becomes milky owing to the formation of insoluble calcium carbonate. This chemical change is a **test for carbon dioxide** (from any source). We express the chemical change thus: —



The two main products of the final chemical change of our digested food are carbon dioxide and water. The carbon dioxide and some water vapor are exhaled from the lungs. The presence of carbon dioxide in exhaled breath may be readily shown by blowing gently through a glass tube into a bottle containing calcium hydroxide (Fig. 19).

Carbon dioxide is also formed by other chemical changes, such as the decay of animal and vegetable matter and the fermentation of organic substances like sugar. The latter

process is illustrated by the liberation of carbon dioxide in making bread.

55. Preparation of carbon dioxide. — We can prepare carbon dioxide by burning carbon, or a combustible compound of carbon, in oxygen or in an ample supply of air. Industrially the gas is manufactured by passing air through hot coke, purifying the gaseous product, and finally extracting the carbon dioxide by a special cooling process. The gas is used in preparing carbonated beverages.

In the laboratory carbon dioxide is most conveniently prepared by the interaction of an acid and a carbonate. The apparatus shown in Fig. 20 can be used for this experiment. Dilute hydrochloric acid and calcium carbonate (in the form of marble chips) are usually used. When the acid is introduced through *B* upon the calcium carbonate in *A*, the gas is rapidly liberated, bubbles up into bottles (previously filled with water), and displaces the water.

The equation for the chemical change in the preparation of carbon dioxide is: —

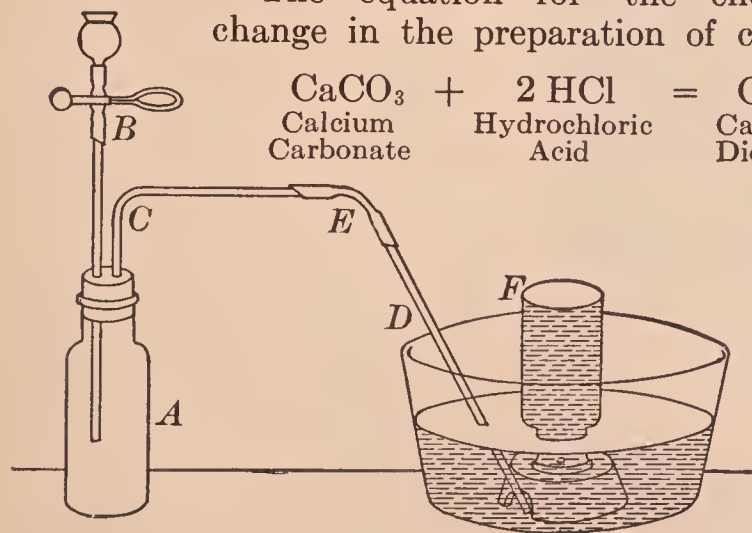
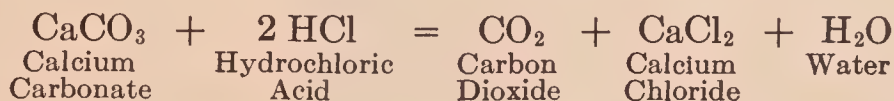


FIG. 20. — Apparatus for preparing carbon dioxide from calcium carbonate and an acid.

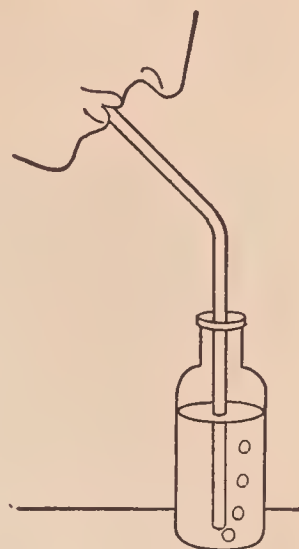


FIG. 19. — Blowing through calcium hydroxide to show the presence of carbon dioxide in the breath.

56. Physical properties of carbon dioxide. — Carbon dioxide is a colorless, odorless gas. It is about 1.5 times heavier than air. A liter of the pure gas weighs 1.98 grams (at 0° C. and 760 mm.).

It dissolves in water. At ordinary temperature and pressure, water dissolves about its own volume of carbon dioxide. Under increased pressure the solubility increases.

The solution of carbon dioxide called **soda water** is manufactured by dissolving carbon dioxide in water. A pressure

of 3 to 4 atmospheres (*i.e.*, 3 to 4 times 760 mm.) is used. When soda water is drawn from a soda fountain or siphon (Fig. 21), the water bubbles and forms a froth, and some gas escapes owing to the diminished pressure. Many beverages,

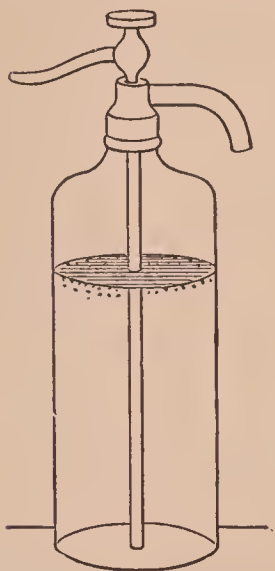


FIG. 21. — A siphon of soda water.

such as ginger ale, are “carbonated,” *i.e.*, they are manufactured by forcing carbon dioxide into the prepared liquid; the bottle is closed tightly with a cap. When the bottle is opened, some of the gas escapes (Fig. 22).

57. Liquid and solid carbon dioxide. — Carbon dioxide can be readily liquefied and solidified. If enough pressure (about 50 atmospheres, *i.e.*, 50×760 mm.) is applied at ordinary temperatures, the gas becomes a liquid. Liquid carbon dioxide is stored and sold in strong metal cylinders. If a cylinder is properly opened, part of the escaping liquid evaporates quickly and removes so much heat that the remainder soon becomes white, snow-like, solid carbon dioxide. Solid carbon dioxide is

an article of commerce, and in some places is delivered in large cakes like ice. It is called “dry ice.” It is also used as a refrigerant in packing and shipping ice cream, butter, eggs, fish, fruits, vegetables, and other perishable goods (Fig. 23).

58. Chemical properties of carbon dioxide. — Carbon dioxide, unlike oxygen, does not assist combustion. Nor does it burn. This negative behavior, so to speak, is sometimes called **inertness** or **stability**. Carbon dioxide is an inert gas.

However, carbon dioxide does react with some substances. Thus, it combines with water to form a compound called **carbonic acid** (H_2CO_3); but this compound is not stable, *i.e.*, it decomposes readily and re-forms water and carbon dioxide.

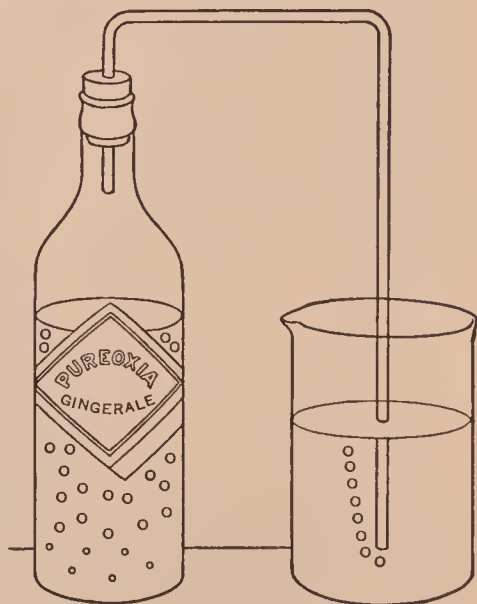


FIG. 22. — Carbon dioxide escaping from a bottle of a carbonated beverage.

We have called attention several times to the reaction in which carbon dioxide and calcium hydroxide form calcium carbonate and water. This chemical change, we have also said, serves as a **test for carbon dioxide**. A similar reaction takes place between carbon dioxide and sodium hydroxide. The product, in this case, however, is **sodium carbonate** (Na_2CO_3), which remains dissolved in the water. The solution feels like wet soap ; in fact, sodium carbonate is sometimes called washing soda and is used in large quantities as a cleansing agent. **Sodium bicarbonate** (NaHCO_3) is closely related to sodium carbonate. Sodium bicarbonate is cooking soda. Alone, or as an ingredient of baking powder, it is widely used in cooking because it gives off carbon dioxide which puffs up the dough.

At high temperatures carbon dioxide reacts with carbon to form monoxide, thus : —



This chemical change takes place in a coal fire (§ 64).

59. Relation of carbon dioxide to life. — Carbon dioxide is not poisonous, though the presence of a small quantity in the air of a room is objectionable. As already stated, the carbon dioxide that is exhaled from our lungs is one of the products formed by the oxidation of the tissues of the body, new tissue itself being formed from the food (§ 34). The carbon needed for the rebuilding of tissue is supplied



FIG. 23. — A cake of solid carbon dioxide for cooling a car of fish.

by fat, meat, sugar, starch, and other foods we eat. Carbon dioxide is a waste product of animal life.

On the other hand, carbon dioxide is an essential food of plants. Through their leaves, especially, they absorb carbon dioxide from the atmosphere, and through their roots they take up water from the soil. These two compounds are transformed by a series of complex changes into oxygen and organic compounds, *e.g.*, starch, sugar, and cellulose. The sunlight and the green coloring matter (called chlorophyll) aid the plant in the formation of these compounds.

The relation of carbon dioxide to life is clear. (1) Plants absorb carbon dioxide and transform it mainly into starch, whereas (2) animals eat starch, or similar food, assimilate it,

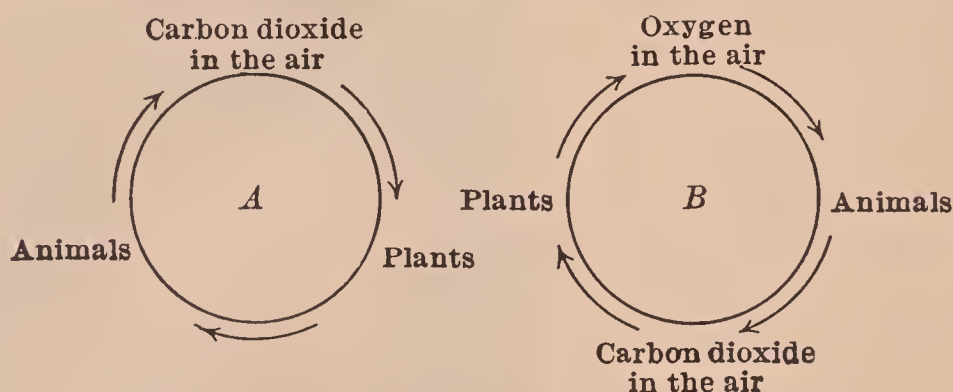


FIG. 24. — Cycle of carbon (A) and oxygen (B).

and oxidize the carbon to carbon dioxide, which is exhaled into the atmosphere ready for the plants again, and so on.

The significant relation of carbon dioxide and oxygen to plants and animals, which is often spoken of as the cycle of carbon and oxygen, is shown in Fig. 24.

60. Carbon dioxide and fire extinguishers. — Carbon dioxide does not burn, but extinguishes burning substances. A saturated solution, instead of the gas itself, is frequently used to put out small fires. The solution is prepared, as needed, in portable fire extinguishers and in chemical engines by the interaction of sulfuric acid and sodium bicarbonate. The ordinary fire extinguisher contains a solution of sodium bicarbonate and a loosely stoppered bottle of concentrated sulfuric acid. When the extinguisher is to be used, the tank is inverted, the glass (or porcelain) stopper of the acid bottle

falls out, the acid mixes with the sodium bicarbonate solution, and the pressure of the generated gas forces the saturated solution of carbon dioxide out of the nozzle of the extinguisher (Fig. 25). Some of the carbon dioxide itself escapes. The water solution of carbon dioxide (together with the gas), if directed upon the base of the fire, forces the oxygen of the

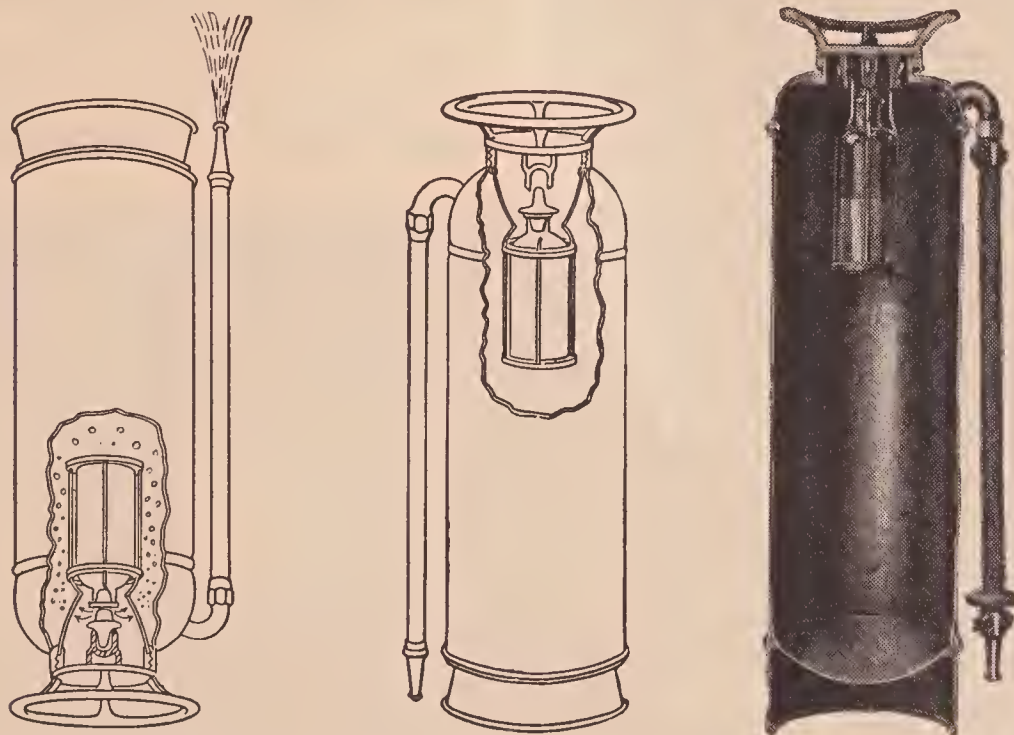


FIG. 25. — Portable fire extinguisher. Right — cut vertically. Middle — partly open, showing stoppered acid bottle in original position. Left — inverted, showing gas bubbles and escaping water.

air away from the fire and reduces, or entirely prevents, combustion.

CARBON MONOXIDE

61. Carbon monoxide differs from carbon dioxide. — Carbon monoxide (CO), like carbon dioxide, is a compound of carbon and oxygen, but the two compounds differ in properties and composition.

Carbon monoxide resembles carbon dioxide in being a gas without color, odor, or taste. But in other properties the two gases differ. Thus, carbon monoxide is only slightly soluble in water, and does not form a compound with water. It is lighter than carbon dioxide; a liter weighs 1.25 gm.

62. Carbon monoxide is poisonous. — Carbon monoxide is an active poison. Moreover it is very dangerous because the lack of odor prevents its detection. A small fraction of one per cent of this gas in the air produces a stupefying effect ; 1 part in 2000 parts of air soon causes unconsciousness, and 1 part in 750 to 800 parts of air will cause death in about half an hour. Many deaths have been caused by breathing air containing this gas.

Carbon monoxide is an active poison because it forms a stable compound with the red coloring matter (hæmoglobin)



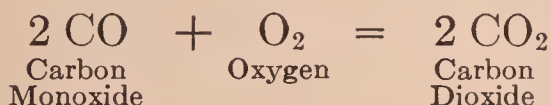
FIG. 26. — Miners testing the air in a mine for carbon monoxide.

of the blood and thereby reduces the amount of oxygen carried by the blood to all parts of the body (§ 34). Hence persons who have been poisoned by carbon monoxide can not usually be revived by air, as in the case of suffocation by carbon dioxide and other gases. The pulmotor is sometimes used to revive persons who have been overcome by gases containing carbon monoxide (§ 36).

Carbon monoxide is an ingredient of ordinary illuminating gas, and also of the gas given off by a charcoal or a coal fire.

Care should always be taken to prevent the escape of illuminating gas and coal gas into rooms occupied by human beings. It is one of the gases produced in mine fires and explosions, and miners wear gas masks in rescue work after an accident (Figs. 26, 27). The exhaust gases from an automobile engine contain carbon monoxide, and special precaution should be taken not to run the engine in a garage or in a poorly ventilated place.

63. Chemical properties of carbon monoxide. — Carbon monoxide, unlike the dioxide, burns in air or oxygen. The flame is blue. The product is carbon dioxide. The equation for this chemical change is: —



The flickering bluish flame often seen on the top of a coal fire is caused by the burning carbon monoxide.

Not only does carbon monoxide unite readily with oxygen, but at a high temperature it withdraws oxygen from oxides. We have already seen that carbon itself acts in the same way (§ 48). We also learned that this chemical removal of oxygen is called **reduction**. For example, in the manufacture of iron from iron ores, the ore, which is an oxide (Fe_2O_3), is reduced by carbon monoxide in a blast furnace, the gas for this purpose being produced by the incomplete combustion of coke.

64. The two carbon oxides are formed in a coal fire. — The oxygen of the air entering at the bottom of a coal fire through the damper at A (Fig. 28) combines with the hot



FIG. 27. — Miner wearing a gas mask and examining his safety lamp.

carbon of the coal and forms carbon dioxide — the *first* change. But the carbon dioxide in passing up through the upper layer of hot coal is reduced by the carbon to carbon monoxide — the *second* change. The carbon monoxide rises through the top of the fire into the air, where some of it escapes up the chimney through the damper at *C*, though much, sometimes all, of it burns with a blue flame and produces carbon dioxide — the *third* change. Therefore we see that the two oxides are closely related chemically and change into one another readily, especially in a coal fire.

65. Formation of carbon monoxide. — Carbon monoxide is always formed when carbon and certain carbon compounds

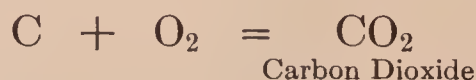
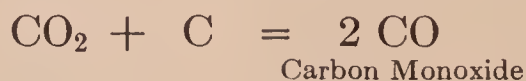
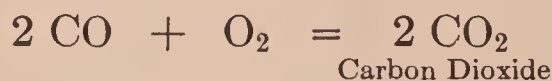
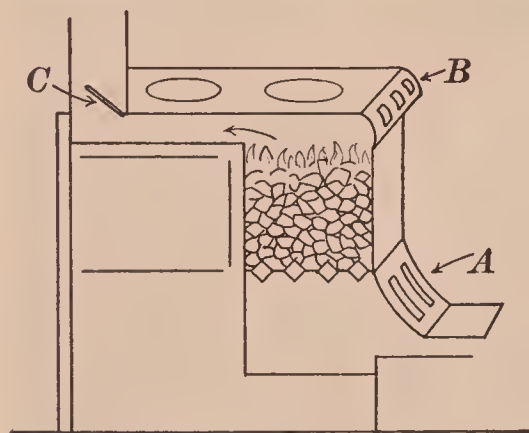


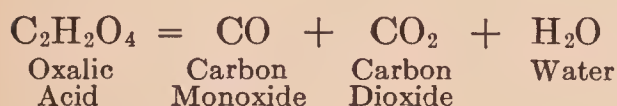
FIG. 28. — The two oxides of carbon are formed in a coal fire.

(*e.g.*, gasolene) burn in a limited supply of air. It is also formed when steam is passed through a hot fire of hard coal or coke. The gaseous product which is called **water gas** is essentially a mixture of carbon monoxide (40 to 50 per cent) and hydrogen (45 to 50 per cent). It burns with a hot flame and is used as a source of heat in industrial plants. When this mixture is enriched by vapor from petroleum oil so that it burns with a yellow flame it is used, alone or with other gases, as illuminating gas. Recall that the carbon monoxide makes such a gas poisonous.

If air is forced through a hot coke fire, or better still if poor-grade coal (*e.g.*, one leaving considerable ash) is burned with a limited supply of air in a special apparatus called a gas-producer (Fig. 29), a mixture of carbon monoxide (about 40 per cent) and nitrogen (about 60 per cent) is formed. It is usually called **producer gas**. If both air and steam are

passed through hot carbon, the gaseous product contains hydrogen besides the carbon monoxide and nitrogen; it is called **modified producer gas**. Producer gas is easily made, burns uniformly and regularly with liberation of considerable heat, leaves no ashes, and is therefore used extensively as a fuel in industrial processes, *e.g.*, in making lime (§ 293) and open-hearth steel (§ 311).

66. Preparation of carbon monoxide. — Carbon monoxide is prepared in the laboratory by decomposing oxalic acid with hot sulfuric acid, thus: —



The carbon dioxide is removed by passing the gases through a solution of sodium hydroxide, and the carbon monoxide is collected in bottles in the usual way.

EXERCISES

1. State the uses of (a) diamond, (b) graphite, (c) coke, (d) charcoal.
2. How is carbon dioxide related to plant and animal life?
3. In what ways can carbon dioxide be prepared? Give equations for the reactions.
4. What is the relation of carbon dioxide to (a) respiration, (b) fermentation of sugar, (c) decay, (d) making lime, (e) combustion?
5. Carbon and carbon monoxide are reducing agents. Explain, and illustrate by equations.
6. Describe fully the action of carbon dioxide on calcium hydroxide. State the reaction by an equation.
7. What is the test for (a) carbon, (b) carbon monoxide, (c) carbon dioxide, (d) a carbonate?
8. State the equation for (a) the oxidation of carbon to carbon monoxide and (b) the reduction of carbon dioxide to carbon monoxide.
9. Define and illustrate reduction.

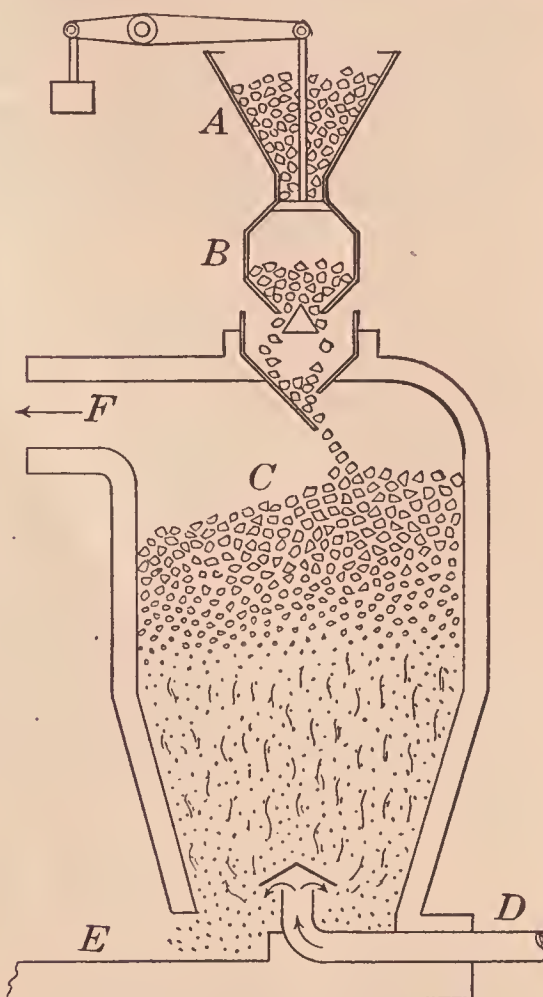


FIG. 29. — Apparatus for manufacturing producer gas. Coal enters through A, B, and air through D into C. Producer gas escapes through F, and ashes are removed at E.

PROBLEMS

1. What is the weight of 10 liters of carbon dioxide?
2. A pupil prepared 5 bottles of carbon dioxide each holding 250 cc. How many gm. of carbon dioxide were prepared?
3. Marble, if treated with acid, yields 44 per cent of its weight as carbon dioxide. If 0.5 kg. of marble was used, how many (a) gm. and (b) l. of carbon dioxide were formed?
4. What weight of marble, 90 per cent pure, is needed to prepare 150 l. of carbon dioxide?

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

- Exercise *5 — Properties of Charcoal.
Exercise *6 — Reduction of Copper Oxide by Carbon.
Exercise *7 — Preparation and Properties of Carbon Dioxide.
Exercise S6 — Combustion and Carbon Dioxide.
Exercise S7 — A Fire Extinguisher and Carbon Dioxide — T.
Exercise 8 — Preparation and Properties of Carbon Monoxide — T.
Exercise S39 — Carbonic Acid — T.
Exercise *48 — Distillation of Soft Coal.
Exercise *49 — Distillation of Wood — T.

SUPPLEMENTARY SECTIONS FROM PART II

- 332.** How coal was formed.
333. Carbon and energy.
334. Carbon dioxide and plants.
(Selections may be made from **383–392.**)

CHAPTER VI

HYDROGEN

67. Occurrence of hydrogen. — Hydrogen, like oxygen, is a gaseous element. It does not occur free to any great extent in nature; natural gas — a mixture of combustible gases which issues from the earth in certain localities — contains about 2 per cent. Contrary to popular belief, the air contains only traces of hydrogen. Vast quantities of free hydrogen exist in the gases that surround the sun. During an eclipse of the sun gigantic streamers of burning hydrogen may be seen shooting out thousands of miles from the sun's disk into space. Mixtures of gases, used for heating, and sometimes lighting, *e.g.*, water gas and producer gas (§ 65), contain from 35 to 50 per cent of hydrogen.

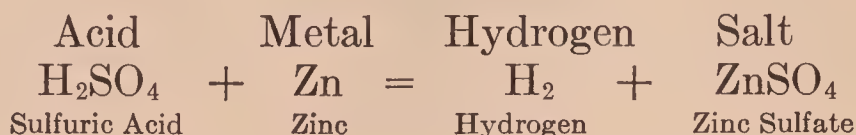
Combined hydrogen is a constituent of many important compounds. Water is 11.18 per cent hydrogen. The human body is about 10 per cent hydrogen. Hydrogen is a constituent of all acids and bases — important classes of compounds to be studied later. (See Chapter XIII.)

All plants and animals contain compounds of hydrogen with carbon and oxygen, and in some cases with nitrogen also. Hydrogen is likewise a constituent of many compounds obtained from animal and plant products, *e.g.*, fat, meat, sugar, starch.

Compounds of hydrogen and carbon form a large and important class of compounds called hydrocarbons, which are ingredients of petroleum (and its products, such as kerosene, gasolene, paraffin, and lubricating oils), illuminating gas, and water gas.

68. Preparation of hydrogen from acids. — Hydrogen is readily prepared by the interaction of certain metals and

compounds of hydrogen called acids. The metals are zinc, iron, or magnesium. Dilute water solutions of the acids are used, *e.g.*, sulfuric acid (H_2SO_4) or hydrochloric acid (HCl). The hydrogen comes from the acid. The metal combines with the rest of the acid to form a compound called a salt, which usually remains dissolved in the liquid. Thus,



In the laboratory hydrogen is usually prepared in a small generator, and collected over water in a pneumatic trough (Fig. 30). Zinc is put in the bottle *A* and acid is introduced through the dropping tube *B* by pressing the clamp. The hydrogen passes out through the delivery tube *D* into the pneumatic trough, bubbles up into the bottles, and displaces the water. No flame should be near during the preparation of hydrogen, because mixtures of hydrogen and air explode when ignited!

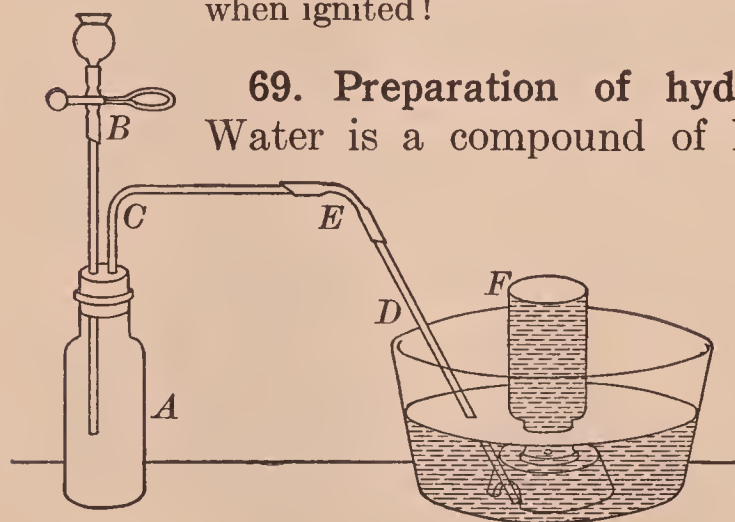


FIG. 30. — Apparatus for preparing hydrogen in the laboratory.

69. Preparation of hydrogen from water. — Water is a compound of hydrogen and oxygen, and hydrogen can be readily prepared from water.

One method has already been described, *viz.*, the electrolysis of water containing a little acid or alkali (§ 22).

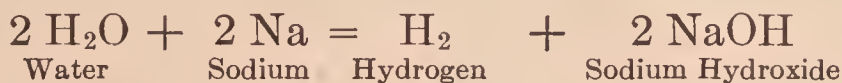
Another method is the interaction of cold water and certain metals. Potassium and sodium interact rapidly and calcium interacts slowly. Potassium interacts so rapidly that the heat ignites the liberated hydrogen, and the hydrogen flame is colored pale violet by the burning vapor of the metal (Fig. 31). But if a small piece of sodium is dropped upon cold water, the sodium melts into a shining globule, which spins about rapidly on the water with a hissing sound and finally disappears with a slight explosion. The heat produced is not sufficient to ignite the hydrogen, unless the water is hot

or the sodium is floated on a piece of filter paper. Then the hydrogen flame is colored yellow by burning sodium. If sodium is wrapped in a piece of fine wire gauze, or of



FIG. 31. — The interaction of water and potassium produces enough heat to ignite the liberated hydrogen.

tea lead pierced with small holes, and then dropped into a dish of water, the hydrogen gas can be collected in an inverted test tube full of water (Fig. 32). The other product of the reaction is sodium hydroxide (NaOH). It is soluble in water, and hence is not seen. But if a piece of red litmus paper is floated on the water, the paper is turned blue by the sodium hydroxide. The equation for the interaction of water and sodium is:



Other metals, *e.g.*, magnesium, zinc, and iron, liberate hydrogen from water only at high temperatures. Thus, hydrogen is liberated when steam — the gaseous form of water — is passed over heated iron. This famous experiment was first performed by the French chemist Lavoisier in 1783, while he was studying the composition of water. He passed steam through a red-hot gun barrel containing bits of iron. The oxygen of the steam combined with the iron, and the hydrogen escaped from the tube. Since Lavoisier was then studying the composition of water, he named the gas hydrogen, which means “water former.”

70. Preparation of hydrogen from bases. — Hydrogen can be prepared by boiling a solution of certain bases with some elements. Bases are compounds of hydrogen, oxygen, and a metal. They are sometimes called **hydroxides**. Hydrogen is liber-

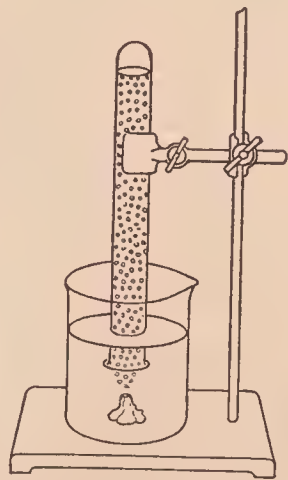
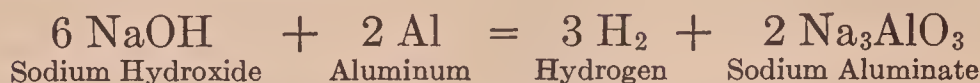


FIG. 32. — Collecting hydrogen formed by the interaction of water and sodium.

ated if sodium hydroxide (NaOH) is boiled with aluminum. The equation is as follows: —



71. Commercial hydrogen. — On a large scale hydrogen is prepared by the electrolysis of water containing an acid or base (§§ 22, 97), by the interaction of iron and sulfuric or acetic acid, and by the reaction between steam and carbon in the manufacture of water gas (§ 387). Considerable is obtained as a by-product in the manufacture of chlorine and sodium hydroxide by the electrolysis of sodium chloride (§§ 121, 285).

72. The preparation of hydrogen illustrates displacement. — The preparation of hydrogen by the interaction of a metal with an acid, water, or a base illustrates **displacement**, or, as it is sometimes called, **substitution** or **replacement**. In the case of zinc and sulfuric acid, the hydrogen is displaced from the acid by the zinc, or the zinc is substituted chemically for the hydrogen. Similarly, hydrogen is displaced (in part) from water by sodium, or sodium is substituted (in part) for the hydrogen of water. Look over the equations again (§§ 68, 69, 70).

We define **displacement** as a chemical change in which one element displaces another from a compound.

Metals differ in their power to displace hydrogen from acids or water. Based on their relative displacing power, they can be arranged in a **hydrogen displacement series**:

Potassium, Sodium, Calcium, Magnesium, Aluminum, Zinc, Iron, Lead, Copper, Mercury, Silver, Gold.

The metals following lead do not displace hydrogen from acids or water. That is, we cannot prepare hydrogen from acids and the metals copper, mercury, silver, and gold. Nor do the metals beyond lead liberate hydrogen from water.

73. Physical properties of hydrogen. — Hydrogen has no taste or color. The pure gas has no odor, though hydrogen as ordinarily prepared has a disagreeable odor, due mainly to impurities in the metals used. Hydrogen is only very slightly soluble in water.

Hydrogen is the lightest known substance. Volume for volume hydrogen is about one fourteenth as heavy as air and one sixteenth as heavy as oxygen. One liter at 0° C. and 760 mm. weighs only 0.09 gm. (exactly 0.08987 gm.). Hydrogen, being so light, diffuses rapidly, *i.e.*, it quickly passes through porous substances (*e.g.*, unglazed porcelain, rubber covering of balloons, and thin sheets of metal). If a bottle of hydrogen is exposed to the air a minute or two, and then a lighted match is dropped in, the match merely burns; if hydrogen were present, a loud explosion would have occurred.

74. Chemical properties of hydrogen. — At ordinary temperatures and under ordinary conditions, hydrogen is not an active element. A mixture of hydrogen and oxygen can be kept indefinitely at the temperature of the laboratory. But if the mixture is heated to about 800° C. or if a flame is brought very near it, the gases unite with a violent explosion.

Under special conditions hydrogen unites with oxygen quietly. Thus, hydrogen burns quietly in oxygen or air if the hydrogen is forced through a small opening and then cautiously ignited.

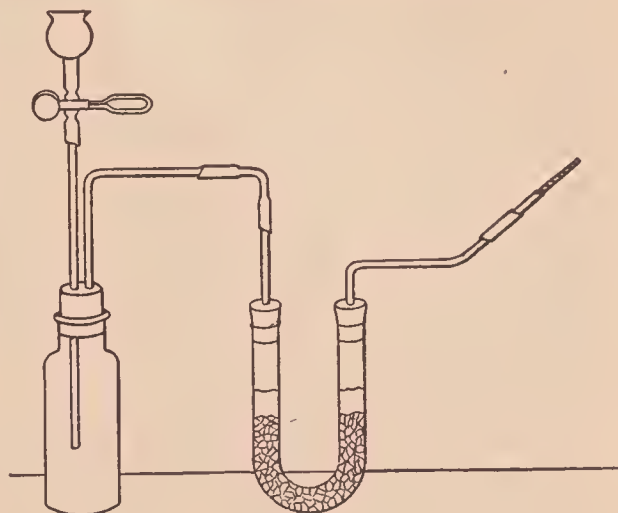
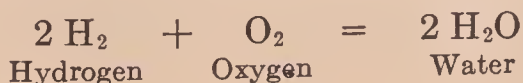


FIG. 33. — Apparatus for burning hydrogen.

To prove this, hydrogen is generated in the apparatus shown in Fig. 33; the gas passes through the drying tube and escapes in a fine stream through the small opening in the platinum tip. After *all* the air has been driven out of the whole apparatus by the hydrogen, the gas is lighted by holding a lighted match at the end of the tip. The flame can hardly be seen and is very hot. If a small, dry, cold bottle is held over the flame, water vapor condenses as a film inside the bottle. That is, hydrogen in burning unites with oxygen, just as other burning substances do. Thus:—



This striking chemical characteristic of hydrogen illustrates the chemical change called combination and also oxidation (§§ 27, 28). The two elements, hydrogen and oxygen, unite to form the compound water; hydrogen is oxidized, and the product might be called hydrogen oxide, though it is called by its more familiar name water.

The film of water that may be seen on the bottom of a vessel placed over a lighted gas range or a Bunsen burner is the condensed vapor formed by the burning hydrogen, and hydrogen compounds, in the illuminating gas. Organic substances containing hydrogen, such as wood and paper, when burned, yield water as one of their products.

Although a small jet of hydrogen when forced out of a generator or a tank of the gas burns quietly in air or in oxygen, a mixture of hydrogen and air burns so rapidly that the combustion is practically an explosion. Therefore the air should be fully expelled from the apparatus in which hydrogen is being generated and all leaky joints should be tightened before the gas is collected; no flames, large or small, should be near. Neglect of these precautions has caused serious accidents.

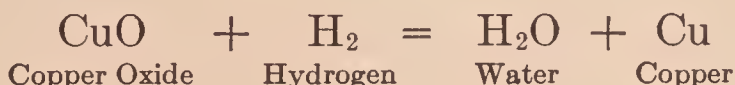
Certain metals under special conditions hasten the rate at which hydrogen combines with elements. Thus, if a mixture of hydrogen and oxygen is passed over finely divided platinum, the gases, which ordinarily would scarcely combine at all, now begin to react to form water. Similarly, hydrogen and nitrogen can be made to unite into the compound ammonia (NH_3), if the mixture is passed under proper conditions over certain metals. In the World War the Germans made ammonia this way, and considerable is manufactured in the United States by this method. The platinum and the other metals, as far as we know now, do not undergo a permanent chemical change in these reactions. They hasten a very slow chemical reaction. A metal, or any other substance, which acts thus is called a **catalyst** or a **catalytic agent** (§ 31). Its function is sometimes compared to that of lubricating oil on a machine. (See also hydrogenation in § 78.)

75. Hydrogen burns but it does not support combustion.

— These facts are illustrated by putting a lighted taper into an inverted bottle of hydrogen (Fig. 34). The taper ignites the hydrogen, which burns at the mouth of the bottle. The taper does not burn inside the bottle, but when it is withdrawn through the burning hydrogen it is relighted.

76. Hydrogen is a reducing agent. — Hydrogen not only combines energetically with free oxygen, but it also withdraws oxygen from compounds. This chemical removal of oxygen, as we learned in § 48, is called **reduction**, and the substances that remove the oxygen are called **reducing agents**. Hydrogen is an energetic reducing agent.

When oxides of certain metals are heated in a current of hydrogen, the oxygen of the oxide is chemically removed and combines with the hydrogen to form water; the metal is left uncombined. Thus, by heating copper oxide in hydrogen, or a gas which contains free hydrogen, *e.g.*, illuminating gas, water and metallic copper are produced. Chemically speaking, the copper oxide is reduced by the hydrogen. The chemical change is also an example of substitution (the hydrogen being substituted for the metal), thus: —



This chemical change can also be interpreted from the standpoint of oxidation, because the hydrogen is oxidized to water at the same time the copper oxide is reduced. In fact, the processes of reduction and oxidation are closely related and either one may be emphasized in interpreting the chemical change. In its simplest form, reduction is the opposite of oxidation. Later we shall see that the terms *oxidation* and *reduction* are both used in a broader sense (§ 317).

77. Test for hydrogen. — A simple test for hydrogen is that it extinguishes a small flame, such as a blazing taper

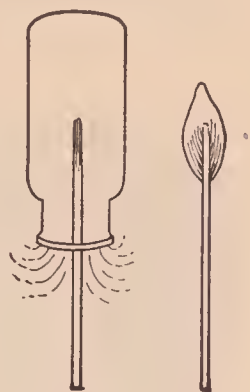
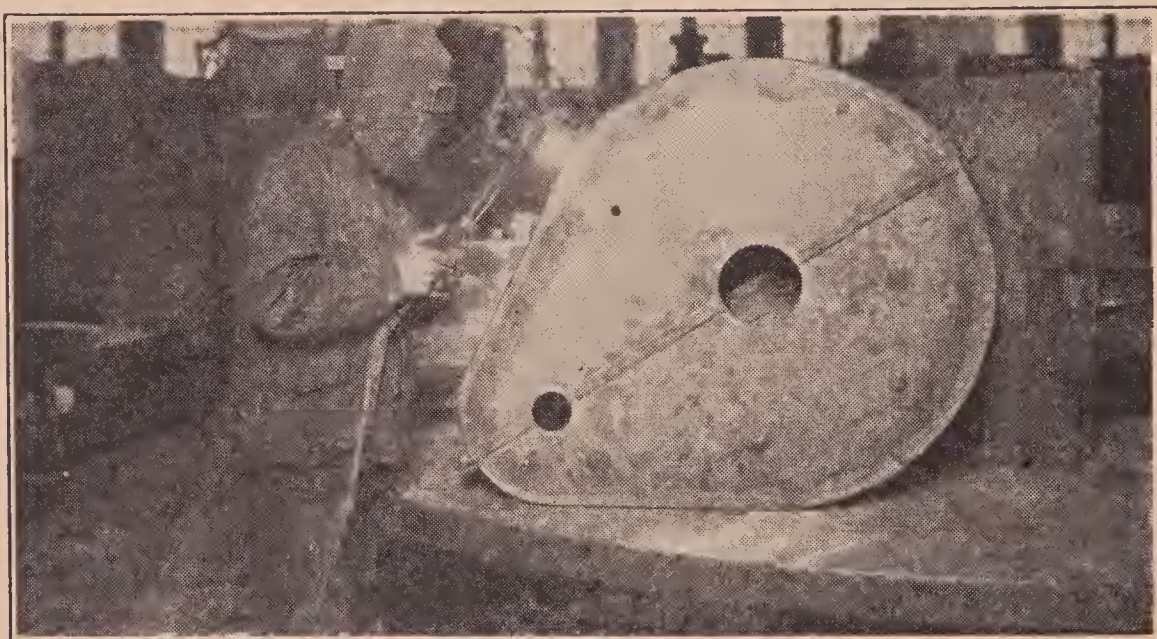


FIG. 34. — Hydrogen burns but does not support combustion.

or joss stick, but is lighted at the same time, often with an explosion, and continues to burn until the gas is exhausted. A conclusive test is that it burns with a colorless, hot flame and forms water as the sole product.

78. Uses of hydrogen. — On account of its extreme lightness, hydrogen is used to fill balloons and some dirigible airships; small balloons are usually filled with coal gas and larger dirigible craft in the United States are filled with the non-combustible gas helium (§ 154).

The intense heat of the hydrogen flame is utilized in the oxy-hydrogen blowpipe. The burner consists of two pointed



Courtesy General Electric Co.

FIG. 35. — Workman welding a gear casing with a flame of atomic hydrogen.

metal tubes. The inner and smaller one is for oxygen, and the outer and larger one for hydrogen; the gases are obtained from tanks and are forced through the small openings of the tubes by the pressure maintained in the tanks. The flame is used to melt quartz and platinum. The oxy-hydrogen flame has been largely replaced by the electric furnace and the oxy-acetylene flame (§ 35). (Acetylene is a compound of carbon and hydrogen — C_2H_2 .)

A special form of hydrogen, called atomic hydrogen, burns with such a hot flame it is used in welding (Fig. 35).

The most extensive use of hydrogen is in transforming

oils into solid edible fats. When certain oils, *e.g.*, cotton-seed oil, are mixed with a small quantity of finely divided nickel, heated, and treated with hydrogen under pressure, the oil and hydrogen unite and form a solid fat. The nickel acts as a catalyst, and is ultimately removed by filtering (from the melted fat). "Crisco" and similar cooking fats are made from cotton-seed oil by this process; objectionable fish oils are also changed into fats suitable for making soap. This chemical change, which consists in the direct chemical addition of hydrogen hastened by a catalyst, is called **hydrogenation**.

EXERCISES

1. How can hydrogen be distinguished from (a) oxygen, (b) carbon monoxide, (c) carbon dioxide, (d) air?
2. Summarize the main physical properties of hydrogen.
3. Why is there danger of an explosion in generating hydrogen? How can the danger be avoided?
4. Define and illustrate (a) reduction and (b) reducing agent. Compare with (a) oxidation and (b) oxidizing agent.
5. State the test for hydrogen.
6. Name the metals in the order of their displacing power.

PROBLEMS

1. Sulfuric acid contains 2.04 per cent of hydrogen. How many grams must be decomposed to yield 85 gm. of hydrogen?
2. Water contains 11.18 per cent of hydrogen. How many gm. of hydrogen can be prepared from 230 gm. of water? How many cc.?
3. A student prepared enough hydrogen to fill six bottles, each holding 250 cc. How many grams were prepared?

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

- Exercise *9 — Preparation and Properties of Hydrogen.
Exercise S8 — Preparation of Hydrogen (Short Method).
Exercise *10 — Reduction of Copper Oxide by Illuminating Gas.
Exercise *11 — Reaction between Sodium and Water — T.
Exercise S9 — Reaction between Zinc and Sulfuric Acid — T.
Exercise S10 — Reduction of Copper Oxide by Hydrogen — T.

SUPPLEMENTARY SECTIONS FROM PART II

- 335. Hydrogen and energy.
- 336. Hydrogenation of fats.

The following sections may be selected from Topic VI: —

- 337. Gases.
- 338. Measuring gases.
- 339. Finding the volume of a gas.
- 340. Law of Charles.
- 341. How we apply the law of Charles.
- 342. Law of Boyle.
- 343. How we apply the law of Boyle.
- 344. How we correct a gas volume for both temperature and pressure.
- 345. Finding the weight of a given volume of a gas.
- 346. Chemical laws and theories.
- 347. The kinetic-molecular theory of the structure of gases.

CHAPTER VII

WATER

79. Distribution of water. — Water is always present in the air as a vapor, which is continually condensing into rain, clouds, mist, fog, dew, hail, frost, or snow. Water occurs as a liquid in vast quantities on and beneath the surface of the earth. As a solid (snow and ice) it covers the tops of high mountains and the polar regions of the globe. Many common foods contain water, often a large per cent, *e.g.*, milk 87, potatoes 78, eggs 73, beefsteak 62. All living things contain water, often to an unusual extent. Thus, the human body is nearly 70 per cent water.

80. Impurities in water. — Water is never found pure in nature. Even **rain water** contains gases and dust washed from the air. When rain strikes the ground, it begins at once to take up impurities from the soil and rocks. Some of the water flows along the surface, becoming more and more impure, and finally reaches the ocean. Some of it soaks into the ground and percolates through the soil. On its journey underground the water dissolves mineral matter and gases. The mineral matter is usually common salt and compounds of calcium, magnesium, and iron; the most common gas is carbon dioxide. If the amount of dissolved matter is so unusual as to give the water a marked taste or medicinal properties, the water is called **mineral water**. Many common mineral waters have limited medicinal value.

Water containing calcium and magnesium compounds is called **hard water**, but in **soft water**, such as rain water, these compounds are absent. **River water** contains earthy impurities brought by the underground and surface water;

it is also often contaminated with compounds formed by the decomposition of animal and vegetable matter (called organic matter), refuse from manufactories, sewage, and harmful bacteria. **Ocean water** contains about 3.5 per cent of dissolved mineral substances, largely common salt and compounds of calcium and magnesium. The peculiar taste of ocean water is due chiefly to these substances.

Besides dissolved mineral matter, water may contain suspended matter, such as fine particles of clay or sand and partly disintegrated organic substances.

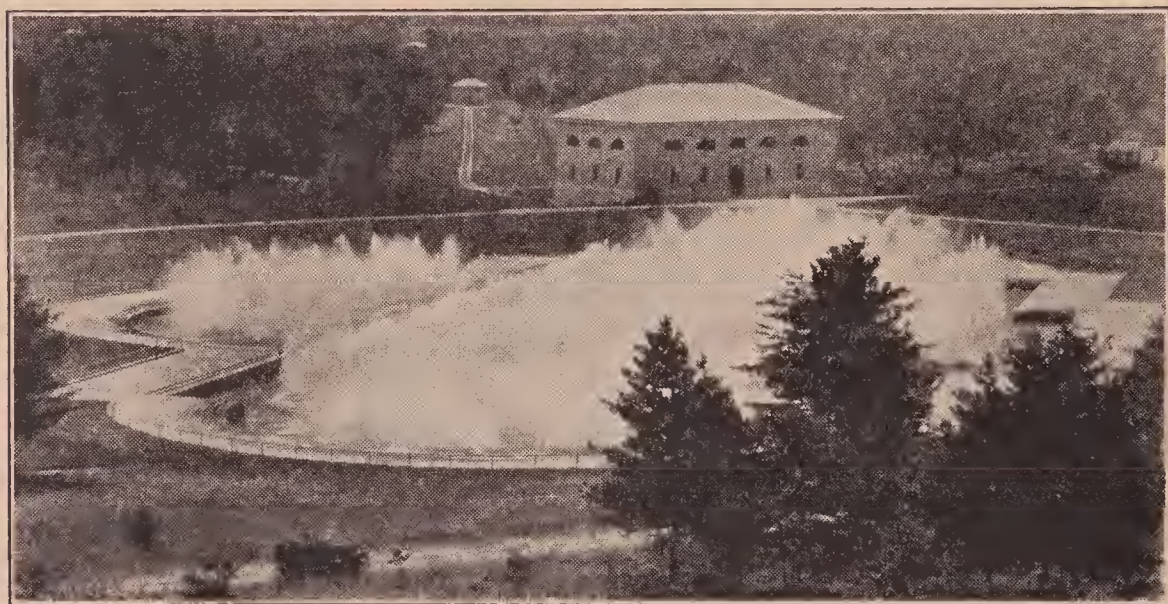


FIG. 36. — Purification of water by spraying it into the air. An aëerator of the New York City water system by which 376 million gallons are purified daily.

81. Purification of water. — It is often necessary to remove certain impurities from water used for drinking and for industries. Thus, water for domestic use should be free from poisons, iron compounds, and as much as possible, magnesium and calcium compounds. And water for steam boilers should be free from calcium and magnesium compounds to prevent the formation of boiler scale (§ 298).

The water used in some towns and cities is purified by **filtering** it slowly on a large scale through layers of sand and gravel. By such a filter, suspended matter is almost completely removed, and certain impurities are decomposed by microorganisms in the upper layer of the filter. A sand

filter must be frequently cleaned. In certain localities the water is **stored** in a large settling basin or reservoir; here the suspended solid matter slowly settles, the process sometimes being hastened or aided by adding aluminum sulfate, which forms a sticky substance to which fine particles cling. In other localities the water is freed from organic matter by **spraying** it into the air (Fig. 36).

The most effective method of destroying organic matter (especially bacteria) in water is by **chemical treatment**. For this purpose chlorine is used. A small amount of liquid

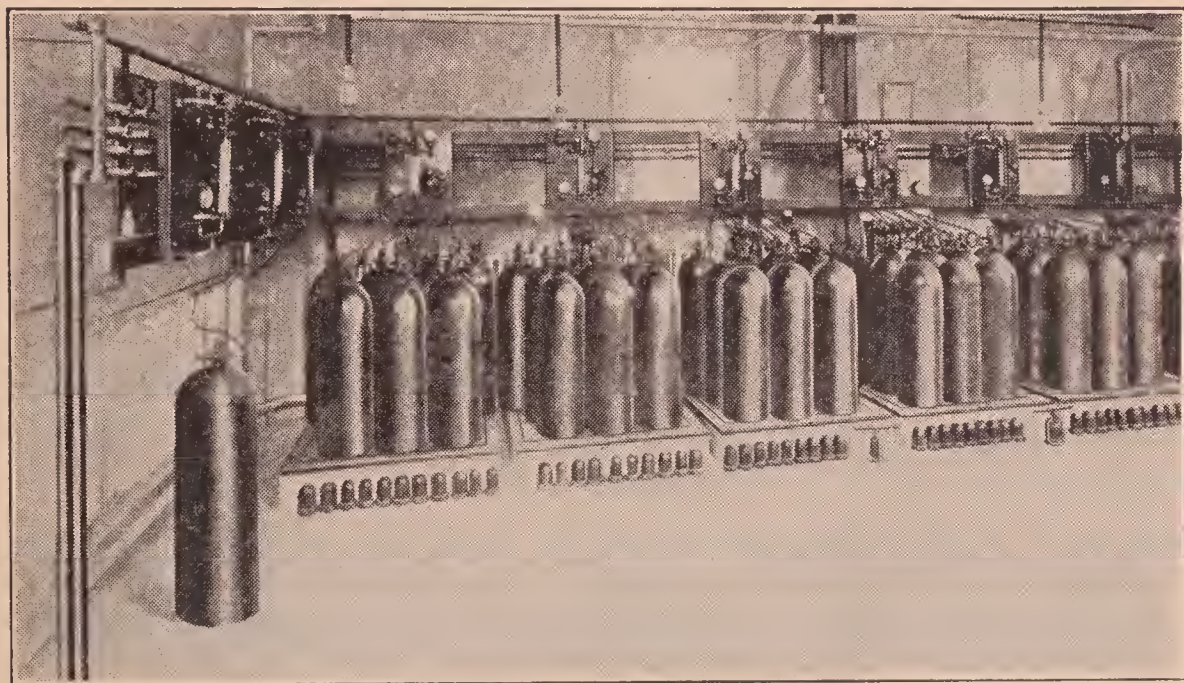


FIG. 37. — Purification of water by chlorine. A chlorinator of the New York City water system by which 400 million gallons are purified daily.

chlorine (about 20 pounds to 1,000,000 gallons of water) is allowed to flow into the entering supply at the pumping station (Fig. 37). The water in a swimming pool can be purified by chlorine: the proportions are about 0.5 pound of chlorine (or 1.5 pounds of bleaching powder) to 100,000 gallons of water.

Water containing bacteria can be purified on a small scale or in an emergency, *e.g.*, for household use during an epidemic, by **boiling** the water ten or fifteen minutes, and then putting it in a bottle or a jar stoppered with cotton. The bottle or jar for keeping the water should be boiled in

water before use. The small filters sometimes used on faucets in the house are not reliable purifiers because they accumulate dirt through which the water must pass.

If the purity of a drinking water is doubtful, a sample should be subjected to a chemical and microscopic examination, supplemented by a rigid sanitary inspection of the surroundings and the source of supply.

82. Distillation. — Water can be purified by **distillation**, *i.e.*, by boiling the water and condensing the steam. By this process the water is separated from suspended and non-

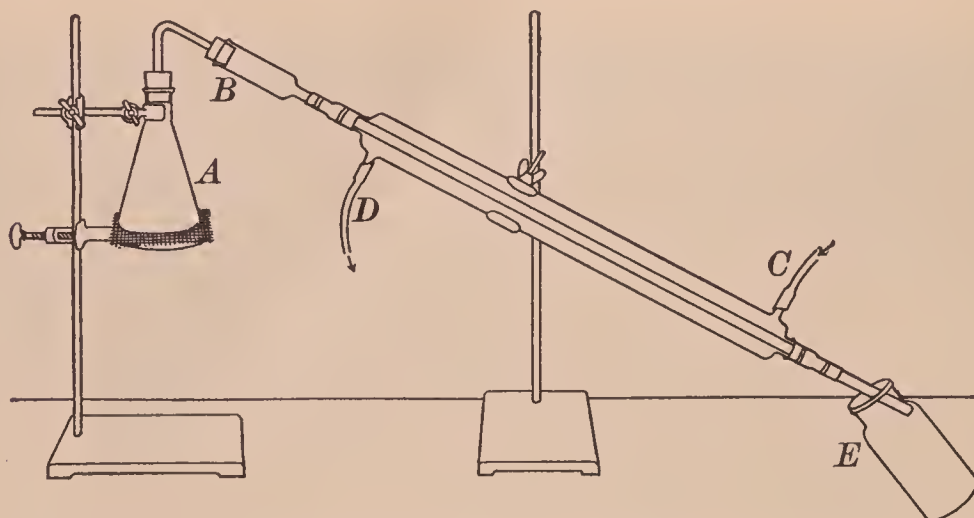


FIG. 38. — Liebig condenser arranged for distillation of water. The vapor from the water boiling in the flask *A* condenses in the inner tube *B*, owing to the decrease in temperature caused by the current of cold water in the outer tube *CD*. The condensed water, called the distillate, drops off the lower end into the receiver *E*, while the non-volatile impurities remain behind in the flask.

volatile impurities, *e.g.*, mineral matter and most organic matter. Water thus purified is called **distilled water**.

Distillation is performed in a condenser. One form, known as the Liebig condenser, is often used in the laboratory (Fig. 38). A simplified distilling apparatus for laboratory use is shown in Fig. 39.

Other forms of apparatus are used, especially for continuous work. One is shown in Figure 40. Cold water enters the condenser *C* at the lower inlet *F*, and is kept level in the chamber *A* by the upper outlet *G*. The chamber *A* is heated by the burner *E*, and steam in passing through *B* and down through the inner tube of the condenser *C* drops off at *D* as dis-

tilled water. Distilled water is prepared on a large scale by boiling water in a metal vessel and condensing the vapor in a block tin or quartz pipe coiled around the inside of a vessel through which a current of cold water is flowing. Glass is not used, because water dissolves traces of substances from the glass and these would contaminate the distilled water.

Distilled water has a flat taste. If it is to be used in making beverages, it is aerated by bubbling air through it; the water soon acquires the accustomed flavor. Much distilled water is used in the

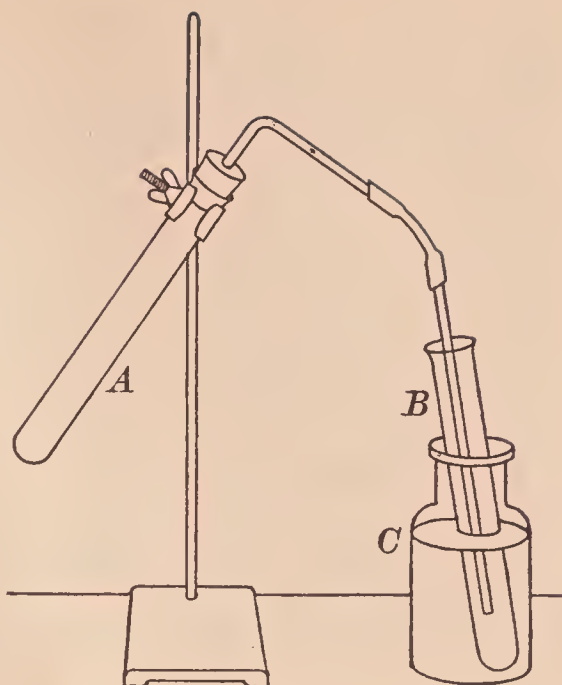


FIG. 39. — Simplified distilling apparatus for use in the laboratory. The water vapor from *A* condenses in *B*, which is cooled by the water in *C*.

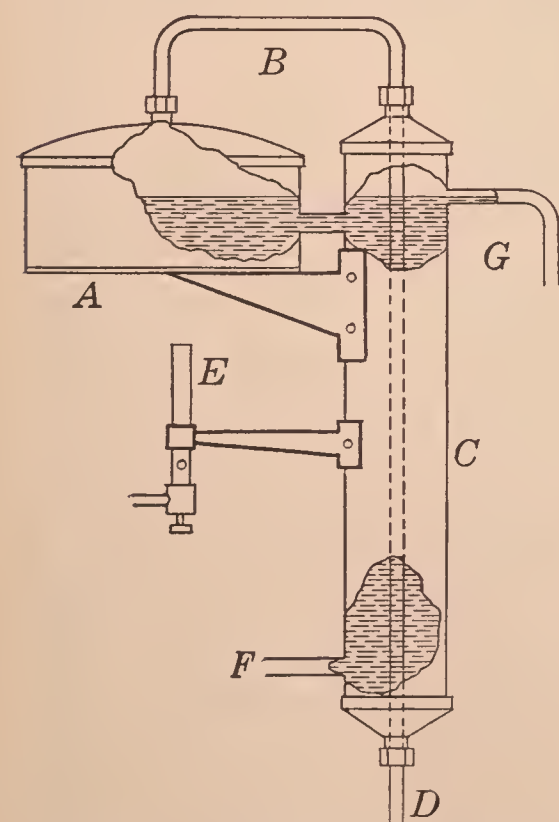


FIG. 40. — Apparatus for distilling water.

chemical laboratory to prepare solutions and in experiments requiring water free from organic and mineral matter. Distilled water is used to prepare medicines which require water free from mineral and organic matter; it is also used in the laboratory to prepare certain solutions, *e.g.*, silver or lead compounds.

83. Some physical properties of water. — At ordinary temperatures pure water is a tasteless and odorless liquid. It is usually colorless, but thick layers are blue. It is a liquid between 0° and 100° C. This means that it freezes at 0° C. and boils at 100° C.

Below the freezing point it is a solid; above the boiling point it is a gas.

Most liquids expand when heated and contract when cooled. But water behaves exceptionally with changes in temperature. If water at 100°C . is gradually cooled, it contracts until 4°C . is reached; if the cooling continues, it expands until 0°C . is reached. Hence at 4°C . a given volume contains the greatest weight of water, *i.e.*, at 4°C . water has its maximum density (Fig. 41).

The density of a liquid is the weight of 1 cc. of the liquid. In the case of water, 1 cc. weighs 0.95838 gm. at 100°C ., 1 gm. at 4°C ., and 0.99987 gm. at 0°C . Since water has its maximum density at 4°C ., the density of water at 4°C .



FIG. 41. — Water has the maximum density at 4°C . In cooling, it contracts between 100° and 4°C ., but expands between 4° and 0°C . Hence a given volume weighs the most at 4°C .

is taken as 1. Water at this temperature is the standard for defining the specific gravity of solids and liquids. By specific gravity we mean the weight of the solid or liquid compared with the weight of an equal volume of water. Thus, the specific gravity of gold is 19, *i.e.*, a piece of gold is 19 times heavier than an equal volume of water at 4°C .

The expansion of water when cooled from 4° to 0°C . is very slight, but the change is exceedingly important in nature. When the water on the surface of a lake or river cools, it contracts, and since it is heavier (volume for volume) than the warmer water beneath, it sinks. The warmer water rises, becomes cool, and likewise sinks, thus causing a circulation which continues until all the water from the surface to the bottom has a temperature of 4°C . If the cooling continues, the surface water expands and remains on the top, because it is lighter than the water beneath. Hence

when the temperature of the air falls to $0^{\circ}\text{C}.$, this upper layer of water freezes and protects the remaining water from the cold air, thus stopping the circulation. Should the circulation continue, as the temperature fell from 4° to $0^{\circ}\text{C}.$, the whole body of water would finally freeze from top to bottom. This condition would not only destroy plants and animals in the water, but would also profoundly affect our climate by the accumulation and slow melting of the ice.

The temperature at which water solidifies or freezes is $0^{\circ}\text{C}.$ (or $32^{\circ}\text{F}.$ — Fahrenheit). This temperature ($0^{\circ}\text{C}.$) is popularly called the freezing point of water. Strictly speaking, the freezing point of water is not the temperature at which ice forms, but the temperature of water in which ice is floating; this temperature is $0^{\circ}\text{C}.$ and stays so until the ice is melted. When water freezes, it expands nearly one-tenth of its volume. More exactly, 100 cc. of water produce 109 cc. of ice. The specific gravity of ice is very nearly 0.92. Hence ice floats in water.

The pressure exerted by water when it expands in freezing is powerful. Vessels or pipes completely filled with water often burst when the water freezes. It is a popular idea that “thawing out” a pipe bursts it. This is not true, because ice contracts when it melts. As a matter of fact, pipes crack as soon as the water freezes, and later when the ice melts, the water flows out of the crack.

When water is heated sufficiently in an open vessel, the liquid becomes a vapor and escapes rapidly. When the temperature of the water reaches $100^{\circ}\text{C}.$ (or $212^{\circ}\text{F}.$), the **water boils**, *i.e.*, it changes rapidly into vapor and the temperature stays at $100^{\circ}\text{C}.$ This vapor is invisible, but as it leaves the vessel it cools and condenses quickly into a cloud of minute drops of liquid water. This cloud is called **steam**.

84. Evaporation. — Liquid water is always changing into water vapor. This process is called **evaporation**. Water vapor is escaping constantly on an enormous scale from the surface of the ocean, lakes, and rivers. On a small scale water vapor is escaping from puddles of water, moist soil, and wet objects. We speak of this process as drying.

85. Chemical properties of water.— We have already seen that water at ordinary temperatures interacts with sodium and potassium, and at higher temperatures with iron (§ 69).

Water combines directly with many oxides. Thus, calcium oxide (CaO) combines with water and forms calcium hydroxide (Ca(OH)_2). Similarly, sulfur dioxide (SO_2) forms the compound sulfurous acid (H_2SO_3). Such oxides are often called anhydrides (see § 219).

Water combines with certain substances and thereby forms compounds called **hydrates**, especially when such substances separate from a solution by crystallization. Thus, from a solution of copper sulfate the blue crystals obtained are a hydrate having the formula $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$. The $5 \text{H}_2\text{O}$ in this formula is separated by a period from the CuSO_4 to indicate that the crystallized solid is a hydrate.

86. Hydrates and water of hydration.— Many familiar substances are hydrates, *e.g.*, washing soda is a hydrate of sodium carbonate and alum of aluminum potassium sulfate. All hydrates, when heated, give up water and form the corresponding anhydrous compound. Thus, the familiar blue solid called copper sulfate is a hydrate ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$) and the gray-white powder formed by heating it is the corresponding anhydrous compound (CuSO_4). Hydrates are made up of two parts, water and the anhydrous substance. The proportion of water of hydration differs in different hydrates. But each hydrate contains an unvarying per cent of water, which is given off on sufficient heating, *e.g.*, hydrate of copper sulfate loses 36.36 per cent. Most hydrates are crystals, often colored, whereas anhydrous substances are usually white, or slightly colored, powders. Anhydrous substances often become readily hydrated again. Thus, when water is poured upon the gray anhydrous copper sulfate, the solid turns blue, and with sufficient water a blue solution is obtained, from which blue crystals of hydrated copper sulfate settle out again.

Some hydrates are so unstable they lose water merely by exposure to air, crumble to a lusterless powder, and, if colored, lose their color. This property is called **efflores-**

cence, and such substances are said to be efflorescent or to effloresce. Washing soda, alum, sodium sulfate, and borax are examples of hydrates which effloresce readily.

87. Water as a solvent. — Water dissolves a great many substances, *i.e.*, they disappear when put into water. The liquid which results from this process of dissolving is called a **solution**. The dissolved substance is called the **solute**, and the water the **solvent**. A water solution of a substance is sometimes called an aqueous solution — the kind we are considering in this chapter.

The degree to which substances dissolve is sometimes called their **solubility** (compare § 90). A solution which contains a small proportion of solute is called **dilute**; one containing a large proportion is called **concentrated**. Addition of water to a solution is called diluting. The partial removal of water by evaporating is called concentrating or evaporating to crystallization; the total removal of water is called evaporating to dryness.

Sometimes the word concentration is used to describe the degree of solubility. If the concentration reaches a maximum at a specified temperature the solution is called **saturated** (compare § 92).

Substances differ widely in their solubility. Some are very soluble, *e.g.*, ammonia (gas), alcohol (liquid), sugar (solid). Others are only very slightly soluble, *e.g.*, hydrogen and oxygen (gases), gasoline and oils (liquids), and sand and limestone (solids). The substances mentioned in the last sentence, and others like them, are often called insoluble because the amount dissolved is insignificant. A large class of substances may be described as moderately soluble.

88. Solutions of gases. — Some gases, like ammonia, are very soluble, while others, such as oxygen and nitrogen, are only slightly soluble. As a rule, the solubility of a gas decreases with rise of temperature. Pressure, too, influences the solubility of gases. Thus, as we have already seen (§ 56), carbon dioxide is forced into cylinders of water in preparing soda water. When the pressure is decreased by opening the valve, the gas escapes rapidly and causes the soda water to froth or foam. Bubbles caused by escaping carbon di-

oxide may also be seen when the cap is removed from a bottle containing a charged beverage (Figs. 21, 22).

This rapid escape of a gas is called **effervescence**. Underground waters often contain considerable carbon dioxide, owing to the great pressure to which subterranean gases are subjected. Hence, many natural mineral waters effervesce when they come to the surface.

89. Solutions of liquids. — Some liquids, such as sulfuric acid, alcohol, and glycerin, dissolve in water in all proportions; others, such as gasolene and kerosene, are very slightly soluble.

Certain liquids dissolve to a limited extent in water. Ether is an example.

90. Solutions of solids. — The solubility of solids in water depends on the substance. Some, like sand, dissolve scarcely at all and are often described as insoluble. Others, like salt, are moderately soluble, while still others, like magnesium chloride or sodium hydroxide, are highly soluble.

The degree of solubility also depends on temperature. Solubility in most cases increases with rise of temperature. A few solids (*e.g.*, calcium hydroxide) are less soluble in hot water than in cold, and a few others (*e.g.*, sodium chloride) dissolve to about the same degree in hot and cold water.

There is a **limit to the solubility** of most substances. As a rule, a given weight of water at a fixed temperature will dissolve only a definite weight of solid; and this is the case, even though more undissolved solid is available for solution. A solution conforming to the conditions just stated is said to be **saturated**. For example, at 20° C. 100 gm. of water dissolve 7.2 gm. of potassium chlorate. This solution is saturated, for if more potassium chlorate is added, it remains undissolved. A saturated solution may also be defined as a solution in which maximum concentration is maintained in contact with some of the undissolved solid.

91. How solubility is expressed. — For ordinary purposes, solubility may be expressed by such general terms as *insoluble*, *slightly soluble*, or *very soluble*. A more accurate way is to state the number of grams of solid dissolved by 100 gm. of water at a fixed temperature, as shown in Table II.

TABLE II. — SOLUBILITY OF SOLIDS IN WATER

SOLIDS	NUMBER OF GRAMS IN SOLUTION IN 100 GRAMS OF WATER		
	10° C.	20° C.	100° C.
Ammonium chloride	33.3	37.2	77.3
Calcium hydroxide	0.176	0.165	0.077
Potassium chloride	31.0	34.0	56.7
Potassium nitrate	20.9	32.0	246.0
Sodium chloride	35.8	36.0	39.0

A useful way of representing solubility is by a **solubility curve**. That is, by a curve drawn through a series of points on cross-section paper, located by finding experimentally the number of grams of the substance soluble in 100 gm. of water at many temperatures. The curves of several substances are shown in Fig. 42. The temperature is read along the vertical lines and the number of grams of solute in 100 gm. of water along the horizontal lines.

Many facts can be read from solubility curves. For example, (1) some substances are very soluble and others only moderately so, (2) the solubility of some substances increases rapidly with rise of temperature, and (3) the increase of solubility of certain substances is slow or slight. So also, if we wish to know the temperature at which a certain number of grams, say 40 gm. of potassium chlorate, are held in solution by 100 gm. of water, we find where the horizontal line numbered 40 cuts the potassium chlorate curve, and then follow the vertical line down to the temperature number, where 80° C. is found.

92. Solution, crystals, and crystallization. — If hot concentrated solutions are cooled, or if enough of the solvent is removed from a cold solution by evaporation, part of the solute separates from the solvent in the solid form, often in beautiful shapes called crystals. The process of separating a dissolved solid from its solution by either of these ways is called **crystallization**. The shape and color of the crystals

are characteristic of the particular substance and serve to identify it. Thus, common salt crystallizes in white cubes.

93. Supersaturated solution. — Crystals are not always deposited from a cooled or a concentrated solution, as just

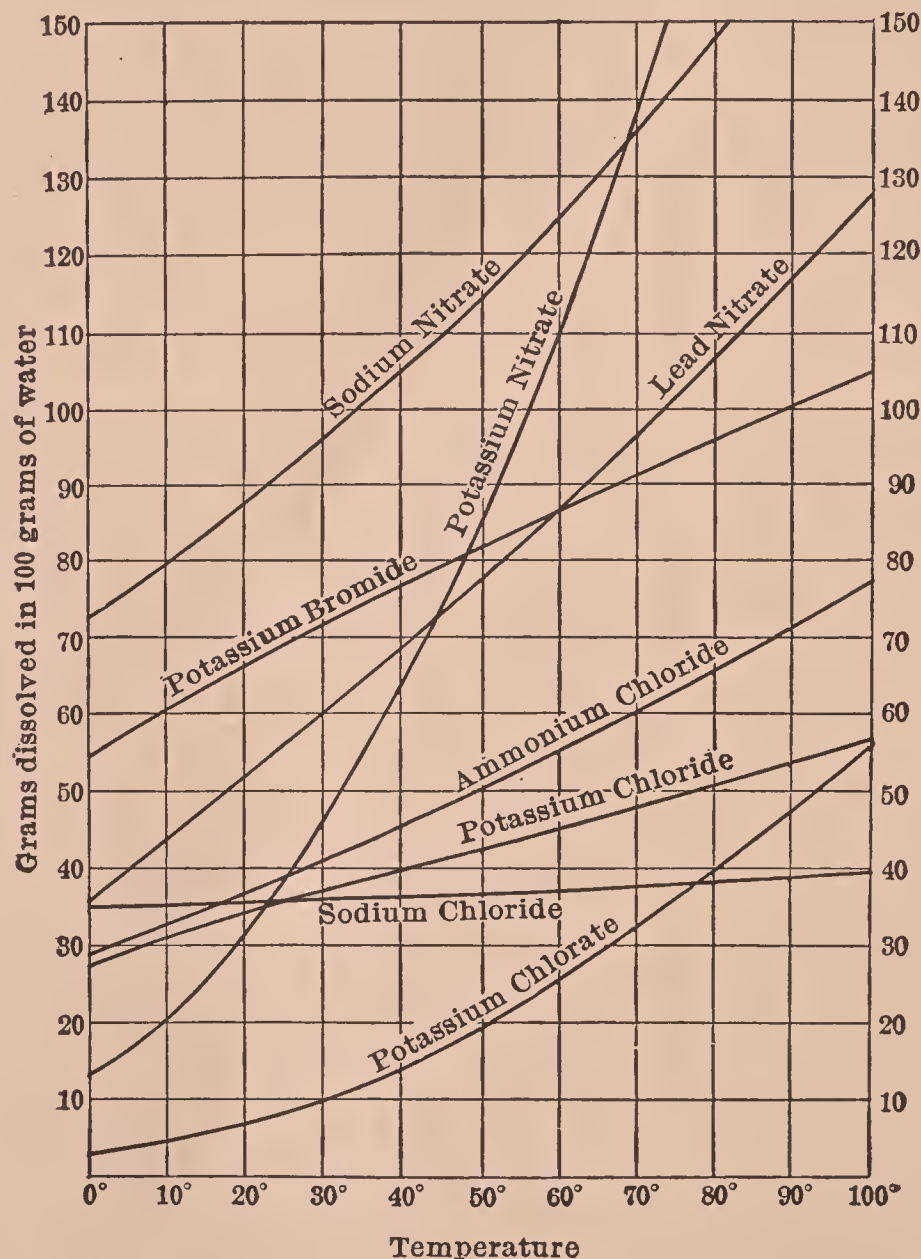


FIG. 42. — Solubility curves.

stated. Thus, a hot, very concentrated solution of some solids, such as sodium sulfate or sodium thiosulfate, deposits no crystals when the *clear* solution cools, although the solution actually contains more solute than the solvent could ordinarily dissolve at the lower temperature! Solutions which contain more solute than is needed for normal satura-

tion are called **supersaturated**. Supersaturation occurs only under special conditions. For example, if a supersaturated solution is stirred or violently shaken, crystals begin to form. Moreover, if a fragment of the solid is dropped into the supersaturated solution, crystals very quickly form upon the fragment and soon accumulate in a conspicuously large quantity.

94. Deliquescence. — Many substances when exposed to air become moist, and sometimes even dissolve in the absorbed water. This property is called **deliquescence** and the substances are said to deliquesce, or to be deliquescent.

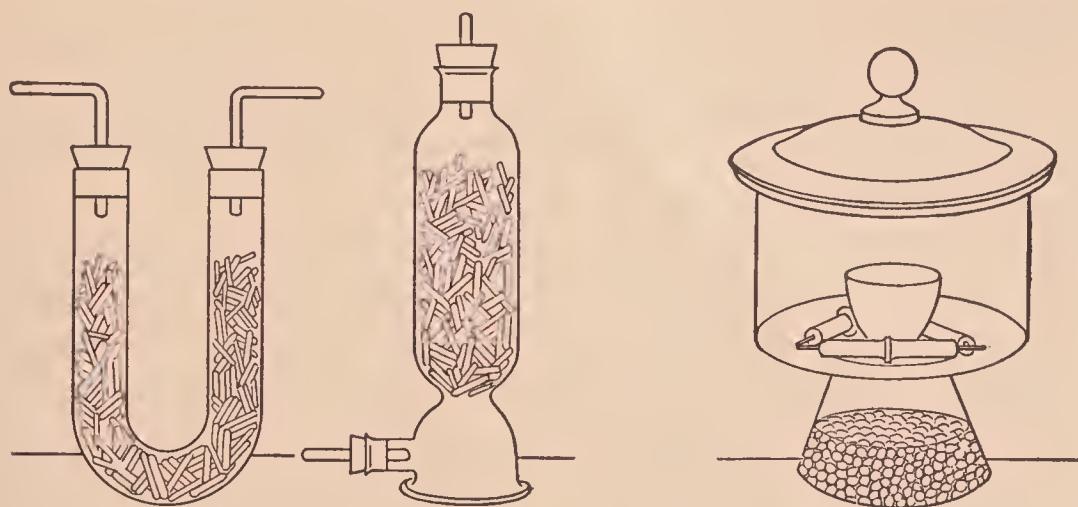


FIG. 43. Apparatus used to dry substances. On the right is a desiccator containing calcium chloride (in the bottom) which dries the substance in the crucible and the air in the desiccator. The other two are used to dry gases.

Deliquescence is a property of very soluble substances. Calcium chloride, potassium carbonate, zinc chloride, sodium hydroxide, and potassium hydroxide belong to this class. Common salt often deliquesces, especially in damp weather, owing to small quantities of magnesium and calcium chlorides which are present as impurities. The property of deliquescence is utilized in the laboratory to dry substances, calcium chloride often being employed for this purpose. Different forms of apparatus are used (Fig. 43).

95. What is a solution? — Let us try three experiments.

(1) If we shake a little salt with water, the salt dissolves. We have a **solution**, *i.e.*, a mixture in which the salt is uniformly distributed and from which the salt will not settle.

(2) If we shake a little powdered starch with cold water, the starch is distributed more or less uniformly throughout the liquid. But on standing, the starch begins to settle, until finally the mixture separates into water and starch. The starch was not dissolved, but merely suspended in the water. Such a mixture of a solid and water is called a **suspension**.

(3) If we shake kerosene vigorously with water, the oil breaks up into fine drops which are distributed throughout the liquid. But after a time the oil separates from the water. Such a mixture of a liquid and water is called an **emulsion**.

Suspensions and emulsions have a common property, *viz.*, the suspended substance in time separates from the water. On the other hand, the dissolved substance does not separate from a solution.

This distinctive property of a solution, *viz.*, non-settling of the solute, is doubtless due to the fact that in a solution the dissolved particles are exceedingly minute — too minute to be seen through a microscope or detected by a beam of light. If a beam of light is passed into a dark room, the path is revealed by the suspended dust particles that reflect the light; this effect may be seen when a sunbeam comes through an opening in a blind or a hole in a curtain. But when a strong beam of light is passed through a solution, no bright path is revealed, because the dissolved particles are very much smaller than dust particles, indeed too small to reflect light.

Certain substances, however, form clear mixtures with water from which the substance does not settle readily, if at all, nor can it be removed by ordinary filtering. These liquids look homogeneous, *i.e.*, they look just alike throughout. And yet, if we pass a beam of light through them, the path is bright, thereby proving that these mixtures contain particles in suspension. Such mixtures are not true solutions, but **colloidal solutions**, *i.e.*, mixtures in which the particles in suspension are very fine — almost as fine as the particles in a true solution. Colloidal solutions should really be called **colloidal suspensions**, but the term colloidal solution

is convenient. Many substances can be reduced to the colloidal state. Such substances are called **colloids**. Typical examples are starch, clay, silicic acid, and metals like gold. (See §§ 261, 446, 498, 511.)

In true solutions, then, the particles of the solute are in an exceedingly fine state of division. Whereas in suspensions and emulsions the particles are much larger — large enough to be seen through a microscope and often with the eye. Between these two classes come colloidal solutions; in them the particles are too fine to settle out, though large enough to reflect light, ranging in size from those in true solutions to those in typical suspensions.

In passing from true solutions through colloidal solutions to ordinary suspensions (and emulsions), the change is gradual, not abrupt, since the distinction is based fundamentally on the size of the particles.

When a colloidal solution is examined through an ultramicroscope (a very powerful microscope arranged for sending a strong light horizontally through the liquid), tiny bright specks are seen darting about in a zigzag motion. These specks are colloidal particles.

The (enlarged) path of one of these points seen in a colloidal solution is complicated (Fig. 44). This motion is called the **Brownian movement** from Robert Brown, the Scotch botanist who first studied it. It is seen in all colloidal solutions regardless of the nature of the particles or the age of the solution. The erratic movement of the colloidal particles is due to the ceaseless, irregular bombardment of the particles by the molecules of water. The movements and the size of the colloidal particles have been carefully investigated, and the results furnish conclusive evidence that the characteristic particles in a true solution are molecules and in a colloidal solution are groups, or aggregates, much larger than molecules.

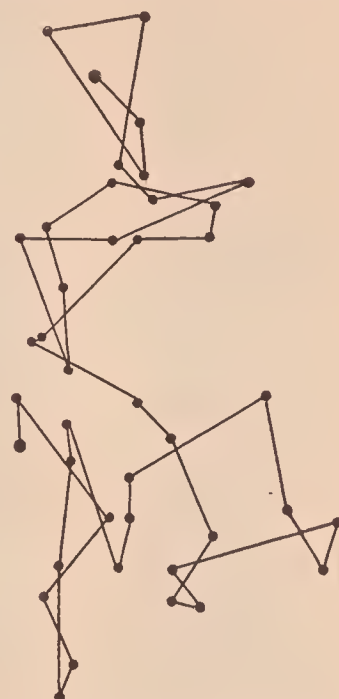


FIG. 44. — Path (enlarged) of a colloidal particle.

96. Composition of water. — Water is a compound of hydrogen and oxygen. That is, its constituents are the elements hydrogen and oxygen, and they are chemically combined in a constant ratio.

We have already learned that hydrogen is one constituent of water. (1) Hydrogen is liberated when certain metals, *e.g.*, sodium, potassium, and iron, interact with water (§ 69). (2) Hydrogen is one of the gases liberated when an electric current is passed through an acid (or an alkaline) solution of water (§§ 22, 69). (3) Hydrogen if burned forms water (H_2O) (§ 75).

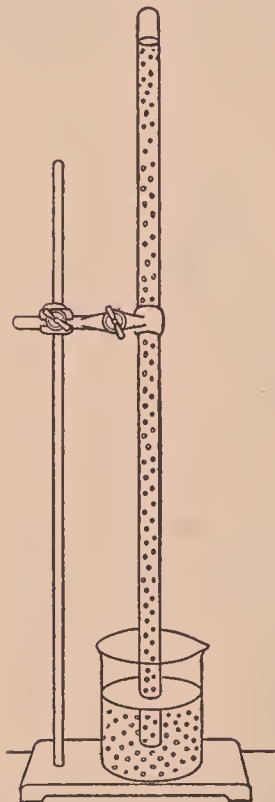


FIG. 45. — Experiment to show that oxygen is one constituent of water.

Similar facts have shown us that oxygen is a constituent of water. (1) Oxygen compounds are formed when metals react with water, *e.g.*, iron and steam form iron oxide and sodium forms sodium hydroxide (§ 69). (2) Oxygen is also liberated when an electric current is passed through water containing an acid (or an alkali) (§ 22). (3) When hydrogen is burned in air or oxygen, water (H_2O) is formed (§ 75). (4) Oxygen is formed when water and chlorine interact.

We can show (4) by a simple experiment. A tube (Fig. 45) about a meter long and closed at one end is completely filled with chlorine water (prepared by saturating water with chlorine) (§ 124.) The open end is immersed in a vessel containing some of the same solution, and the whole apparatus is placed in the direct sunlight. The chlorine and water interact. Bubbles of gas soon appear in the liquid, and after a few hours a small volume of gas collects at the top of the tube (Fig. 45). The gas can be shown to be oxygen by the usual test, *viz.*, relighting a glowing joss stick or a splint of wood.

97. Electrolysis of water. — Pure water does not conduct electricity, but a solution containing an acid, a base (*e.g.*, sodium hydroxide), or a salt (*e.g.*, sodium chloride) does conduct electricity. The decomposition of such a water solution by electricity, called traditionally the electrolysis

of water, shows by a single experiment that water consists of hydrogen and oxygen.

It can be done in a special form of apparatus called the Hofmann apparatus (Fig. 46).

A mixture of water (10 vols.) and concentrated sulphuric acid (1 vol.) is poured into the apparatus until the reservoir is half full (after the stopcocks have been closed).

The electric current may be obtained from a 6-volt storage battery, or four dry cells connected in series, or a direct street current reduced by two 50-watt lamps. The wires are connected with the piece of platinum near the bottom of each tube, and as soon as the current passes, bubbles of gas appear on the platinum, rise, collect in the upper part of the tubes, and slowly force liquid from each tube up into the reservoir.

The current should be shut off when the tube containing the larger volume of gas is about three-fourths full. Assuming that the tubes have the same diameter, the gas volumes are in the same ratio as their heights, which will be found by measurement to be approximately two to one. Tests applied to each gas (by letting a little out through the stopcock) show that the gas having the larger volume is hydrogen and that the other gas is oxygen.

98. How the exact composition of water is found. — The experiments just cited and described show the **qualitative composition** of water. That is, they show that water is a compound of the two elements hydrogen and oxygen. But they give us no information about the proportion of the elements in the compound. To find the **quantitative composition** of water, we must study the results of experiments performed for the purpose of determining the exact proportions — “the quantity” — in which the two elements combine to form the compound.

Exceptionally accurate determinations of the composition of water were completed by the American chemist Morley in 1895 (Fig. 47) after twelve years of labor. In his experiments he not only measured the hydrogen and oxygen that combined but he also weighed them and the water formed by

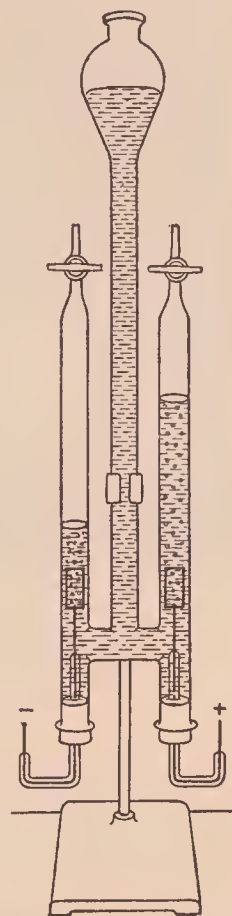


FIG. 46. — Electrolysis of water (containing sulphuric acid).

combining them. Morley found (1) 1 part by weight of hydrogen combines with 7.9395 parts by weight of oxygen and (2) hydrogen and oxygen unite in the ratio of 2.00268 to 1 by volume.

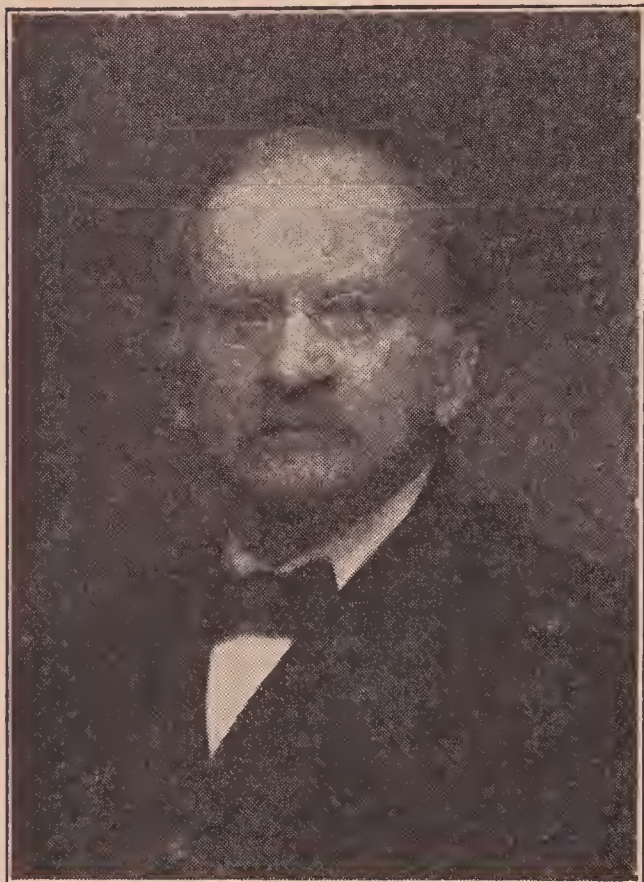


FIG. 47. — The American chemist Morley (1838-1923), who made a very accurate study of the composition of water.

has only historical interest. However, the method can be readily duplicated in our laboratories.

99. Dumas' determination of the gravimetric composition of water. — Another method was used by the French chemist Dumas in 1843. It consisted in passing dry hydrogen over heated copper oxide. We have seen (§ 76) that in this chemical change hydrogen reduces copper oxide and thereby forms copper and water. If the copper oxide and copper are weighed, the loss is the weight of the oxygen used. If the water is collected and weighed, the difference between the weights of the water formed and the oxygen used is the weight of the hydrogen. The result obtained by Dumas while accurate for those days, now

100. Summary of the composition of water. — Experiments show that water consists of the two elements hydrogen and oxygen combined in a fixed ratio by weight, *viz.*, 1 to 7.9395; they are also combined in the ratio of 2.00268 to 1 by volume. Usually these ratios are stated approximately as 2 to 16 by weight and 2 to 1 by volume. Often the gravimetric composition of water is stated in per cent, *viz.*, 11.18 per cent of hydrogen and 88.82 per cent of oxygen. Sometimes, we say, briefly, water is $\frac{1}{9}$ hydrogen and $\frac{8}{9}$ oxygen.

EXERCISES

1. State three ways by which drinking water can be purified.
2. Describe distillation. Sketch a Liebig condenser.
3. State four important physical properties of water.
4. As in Exercise 3, chemical properties.
5. Define and illustrate (a) water of hydration, (b) efflorescence, (c) anhydrous, (d) hydrate.
6. Define and illustrate (a) solution, (b) solvent, (c) solute, (d) saturated solution.
7. Define and illustrate deliquescence. How does it differ from efflorescence and effervescence? What common substances (a) effloresce and (b) deliquesce?
8. At what temperature does water (a) boil and (b) freeze?
9. Describe experiments which show that hydrogen and oxygen are components of water.
10. What is the composition of water by weight and by volume?

PROBLEMS

1. If 5 gm. of crystallized aluminum sulfate lose 2.43 gm. on heating, what per cent of water of hydration does this crystallized substance contain?
2. By the use of the solubility curves in Fig. 42 answer the following: (a) How many gm. of sodium chloride are in solution at 20°, 30°, 55°, 65°, 0°, 100°? (b) At what temperatures are 60 gm. and 95 gm. of potassium bromide in solution? (c) How much sodium nitrate is in solution at 20°, 25°, 30°? (d) As in (c), how much potassium bromide?
3. How much (a) oxygen and (b) hydrogen could be obtained from 25 gm. of water?

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

- Exercise 12 — Purifying Water by Distillation.
Exercise S 11 — Preparation and Properties of Distilled Water — T.
Exercise *13 — Suspension and Solution of Solids.
Exercise *14 — Effect of Heat on the Solubility of Solids.
Exercise *15 — Formation of Crystals.
Exercise *16 — Effect of Shape on the Solubility of a Solid — T.
Exercise *17 — Water of Hydration.
Exercise S 13 — Anhydrous Compounds.
Exercise *18 — Per Cent of Water of Hydration.
Exercise 19 — Electrolysis of Water (Acid Solution) — T.

Note: Exercises S 12 — T, S 14 — T to S 17 — T may be done at this time or postponed till the corresponding subjects are studied in Topic VIII, Part II.

SUPPLEMENTARY SECTIONS FROM PART II

- 348. Vapor pressure.
- 349. Efflorescence and vapor pressure.
- 350. Deliquescence and vapor pressure.
- 351. Volumetric composition of water.
- 352. Gay-Lussac's law of gas volumes.

CHAPTER VIII

SYMBOLS AND FORMULAS

101. What symbols mean. — Each chemical element is designated by a symbol (§ 14), which is an abbreviation of its name. Thus, O is the symbol of oxygen, C of carbon, H of hydrogen. The symbols of the elements are given in the Table on the back inside cover. These symbols were introduced and first used extensively by the Swedish chemist Berzelius (Fig. 48) about 1811. He analyzed many substances and used the symbols to show the composition of compounds and to express the relations of elements and compounds in chemical changes.

Each symbol also stands for one atom of an element. Thus, H means one atom of hydrogen. More than one free atom is designated by writing the proper numeral before the symbol. Thus, 2 H means 2 free atoms of hydrogen. To represent atoms in chemical combination, a subscript is used. Thus, H_2 means 2 combined atoms of



FIG. 48. — The Swedish chemist Berzelius (1779–1848), who introduced and first used the symbols of the elements.

hydrogen, as in H_2O , H_2SO_4 . Similarly, NH_3 means 3 atoms of hydrogen combined with 1 atom of nitrogen.

Each symbol also expresses the atomic weight of the element. Thus, O represents one atom of oxygen which has the atomic weight 16; similarly, $\text{H} = 1$, $\text{C} = 12$, $\text{N} = 14$ (see Table on inside of back cover).

To sum up, a symbol has these meanings: (1) an element, (2) one atom of an element, (3) the atomic weight of an element.

102. What are chemical formulas? — A formula is a group of symbols which expresses the composition of a compound (§§ 11 (3), 15). Thus, H_2O is the formula of water, CuO of copper oxide, NH_3 of ammonia. In writing a formula, the correct number of symbols of the atoms making up a molecule of the compound is placed side by side. Thus, CO is the formula of carbon monoxide, because 1 molecule of this compound consists of 1 atom each of carbon and oxygen. Whereas, CO_2 is the formula of carbon dioxide, because 1 molecule is composed of 1 atom of carbon and 2 atoms of oxygen. The symbols making up a formula might be written in different orders, but usage has determined the order in most cases.

A formula represents one molecule. To designate several molecules, we place the proper numeral before the formula. Thus, KClO_3 means 1 molecule and 2KClO_3 means 2 molecules of potassium chlorate.

In some compounds certain atoms in a molecule act as a group in chemical changes. This fact is expressed by inclosing the group in a parenthesis, *e.g.*, calcium hydroxide has the formula $\text{Ca}(\text{OH})_2$ because the group OH usually acts as a unit. Such groups are often called radicals. Thus, OH is the hydroxyl radical, SO_4 the sulfate radical, and NH_4 the ammonium radical. Sometimes the parenthesis is replaced by a period, *e.g.*, $\text{C}_2\text{H}_5.\text{OH}$ (ethyl hydroxide) and $\text{CuSO}_4.5 \text{H}_2\text{O}$ (copper sulfate pentahydrate (§ 86)). The period and parenthesis are usually omitted from the formulas of familiar compounds, *e.g.*, ammonium hydroxide, NH_4OH .

In some formulas a group is placed inside a parenthesis,

e.g., $\text{Pb}(\text{NO}_3)_2$. This means that the group NO_3 , in this case, is to be multiplied by 2. The expression $2 \text{Pb}(\text{NO}_3)_2$ means that the whole formula must be multiplied by 2. That is, in 2 molecules of lead nitrate there are 2 atoms of lead, 4 of nitrogen, and 12 of oxygen.

103. Relation between formulas and molecular weights.

— Since a symbol stands for the atomic weight of an element, a formula stands for the sum of the atomic weights represented by the group of symbols. This sum is called the molecular weight. In a few words, a symbol stands for an atomic weight and a formula stands for a molecular weight. Thus, the symbols H and Cl stand for the atomic weights 1 and 35.5 respectively, and the formula HCl stands for their sum $1 + 35.5$, or 36.5. If we know the formula of a compound, a simple way of finding the molecular weight is to add the atomic weights corresponding to the atoms in the formula. Using approximate values, the molecular weight of water (H_2O) is $2 + 16 = 18$. Similarly, the molecular weight of lead nitrate ($\text{Pb}(\text{NO}_3)_2$) is $207 + 2(14 + 48) = 331$. Atomic weights are given in the Table on the inside back cover of this book.

104. Relation between the formula and the percentage composition of a compound. — The composition of a compound can be expressed by a formula and also in per cent (§ 11). The “composition in per cent” is often called “percentage composition.” Thus, we can express the composition of water by the formula H_2O , and also by hydrogen = 11.18 per cent and oxygen = 88.82 per cent.

How are formulas and per cents related? The answer is simple. The symbols in the formula stand for numbers, and the composition in per cent is the mathematical equivalent of the chemical formula.

The formula of potassium chlorate is KClO_3 . Suppose we wish to express the composition in per cent. The process consists in transposing the chemical formula KClO_3 into the equivalent mathematical expression. There are three steps: —

(1) Find the molecular weight by adding the atomic weights.

(2) Divide the weight of each element by the total molecular weight,

(3) Multiply each quotient by 100.

Proceeding as above, we have (1) $K = 39$, $Cl = 35.5$, and $3 O = 48$ (*i.e.*, 3×16), and the molecular weight is their sum, 122.5.

(2) and (3).

$39 \div 122.5 = 0.3184$, and $0.3184 \times 100 = 31.84\%$ of K.

$35.5 \div 122.5 = 0.2898$, and $0.2898 \times 100 = 28.98\%$ of Cl.

$48 \div 122.5 = 0.3918$, and $0.3918 \times 100 = 39.18\%$ of O.

This process of finding the composition in per cent from the formula is often called **calculating the percentage composition** of a compound.

105. The simplest formula of a compound can be calculated from its percentage composition. — The calculation of a formula from the percentage composition is simply the reverse of the process given in § 104, *i.e.*, thus: —

(1) Divide each per cent by the corresponding (single) atomic weight.

(2) Reduce the quotients to whole numbers.

(3) Write the formula.

Let us take an example. The composition of sulfuric acid is hydrogen = 2.04 per cent, sulfur = 32.65 per cent, oxygen = 65.31 per cent.

(1) Dividing the percentage of each element by the corresponding atomic weight, the quotients are 2.04, 1.02, and 4.08.

(2) Reducing these quotients to whole numbers (by dividing by 1.02 in this case), the final quotients are 2, 1, 4.

(3) These quotients represent the number of atomic weights of the respective elements in a molecule of this compound. And since atomic weights and atoms are represented by symbols, a molecule of sulfuric acid contains 2 atoms of hydrogen (2 H), 1 of sulfur (S), and 4 of oxygen (4 O). This means that the formula of sulfuric acid must be H_2SO_4 .

Formulas calculated by this method are often the simplest formulas of the corresponding compound.

EXERCISES

1. Learn the symbols of these elements: (a) Aluminum, calcium, carbon, chlorine, copper. (b) Hydrogen, iron, lead, magnesium, mercury, nitrogen, oxygen. (c) Phosphorus, potassium, silicon, silver, sodium, sulfur, zinc.

2. What elements correspond to C, Cl, Ca, Cu, S, Si, Mg, Hg, H?

3. What do these mean? H, H_2 , 2 H, 2 O_2 , Cl, Cl_2 , 3 Cl, 3 Cl_2 , N_2 , K, 2 Ca, 3 Fe, S_2 , Cu, Al_2 .

4. What do these mean? H_2O , 2 H_2O , KNO_3 , 4 H_2SO_4 , NaOH, 3 $Ca(OH)_2$, HNO_3 , $BaCl_2 \cdot 2 H_2O$, 2 FeS, 3 $CaCl_2$.

(HINT. H_2O means 1 molecule of water containing 2 atoms of hydrogen combined with 1 atom of oxygen.)

5. What is the formula of water, potassium chlorate, sulfuric acid, magnesium oxide, copper oxide, sodium hydroxide? What is the molecular weight of each?

PROBLEMS

(Some of these problems may be used in subsequent assignments.)

1. Calculate the molecular weight (or multimolecular weight) of the following compounds by finding the sum of the atomic weights: (a) magnesium oxide (MgO), (b) hydrogen peroxide (H_2O_2), (c) zinc chloride ($ZnCl_2$), (d) 2 $Cu(NO_3)_2$, (e) 3 $Al_2(SO_4)_3$, (f) $FeSO_4 \cdot 7 H_2O$.

2. Calculate the simplest formula of each compound from the indicated percentage composition: (a) Cl = 60.68, Na = 39.31; (b) S = 23.52, Ca = 29.41, O = 47.05; (c) C = 40, H = 6.67, O = 53.33.

3. As in Problem 2: (a) N = 26.17, H = 7.48, Cl = 66.35; (b) As = 75.8, O = 24.2; (c) N = 82.35, H = 17.65.

4. As in Problem 2: (a) Si = 19.5, C = 66.62, H = 13.88; (b) Ca = 38.71, P = 20, O = 41.29; (c) H = 1, K = 39.06, C = 11.99, O = 47.95.

5. Calculate the formula of a compound 18 gm. of which contain 8.4 gm. of iron and 9.6 gm. of sulfur.

6. As in Problem 5: 0.84 gm. contain 0.587 gm. of iron and 0.253 gm. of oxygen.

7. Calculate the percentage composition of (a) hydrochloric acid, (b) hydrogen sulfide (H_2S), (c) ammonia (NH_3), (d) hydrogen peroxide (H_2O_2).

8. As in Problem 7: (a) calcium oxide (CaO), (b) calcium carbonate ($CaCO_3$), (c) calcium sulfate ($CaSO_4$), (d) calcium fluoride (CaF_2).

9. As in Problem 7: (a) cane sugar ($C_{12}H_{22}O_{11}$) and (b) grape sugar ($C_6H_{12}O_6$).

10. As in Problem 7: (a) sodium phosphate (Na_3PO_4), (b) disodium phosphate (Na_2HPO_4), (c) monosodium phosphate (NaH_2PO_4), (d) phosphoric acid (H_3PO_4).

11. Calculate the per cent of (a) copper and (b) water in crystallized copper sulfate ($CuSO_4 \cdot 5 H_2O$).

SUPPLEMENTARY SECTIONS FROM PART II

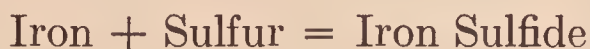
- 353. Facts, laws, and theories (see § 346).
- 354. Law of the conservation of matter.
- 355. Law of constant composition.
- 356. The atomic theory.
- 357. Atoms and molecules.
- 358. Interpretation of chemical change by the atomic theory.
- 359. How the atomic theory helps us explain fundamental laws.
- 360. Atomic weights.
- 361. Equivalent weights.
- 362. The difference between equivalent and atomic weights.

CHAPTER IX

CHEMICAL REACTIONS — EQUATIONS — CALCULATIONS

106. Chemical reactions. — A chemical change is called a chemical reaction, an interaction, or simply a **reaction**.

107. What is a chemical equation? — We learned in § 17 that a reaction can be represented in a condensed form by a verbal equation. Thus: —



In §§ 14, 15 we learned that elements and compounds are represented by symbols and formulas. Therefore, we can use symbols and formulas in place of words. The above equation then becomes: —



108. How to read an equation. — The plus (+) sign may be read *and* or *plus* and the equality (=) sign *form(s)*, *give(s)*, *yield(s)*, or *equal(s)*. An arrow (\rightarrow) is sometimes used instead of the equality sign (=); both signs are read in the same way. Since equations are really expressions of equality between two total weights, the sign of equality is the proper sign to use. (However, see § 192.)

Consider the equation:



This equation may be read in several ways: —

(1) Zinc and sulfuric acid form (or give) hydrogen and zinc sulfate.

(2) Zinc plus sulfuric acid equal hydrogen plus zinc sulfate.

(3) One atom of zinc and one molecule of sulfuric acid form one molecule of hydrogen and one molecule of zinc sulfate.

(4) Anticipating a little (§ 112), 65 parts of zinc interact with 98 parts of sulfuric acid and yield 2 parts of hydrogen and 161 parts of zinc sulfate, all parts by weight.

109. How to write an equation. — The simplest way is to substitute symbols and formulas for the names of substances. But the mere change of words to symbols and formulas would not always give a correct equation. So these steps should be followed in writing an equation : —

(1) Find (in the Table of atomic weights or in the text (by the Index)) the correct symbol or formula of each substance involved in the reaction.

(2) Write a preliminary equation by putting on the left (of the equality sign) the symbol or formula of each factor, *i.e.*, the original, initial, or reacting substances, and on the right the symbol or formula of each product (*i.e.*, the final substances).

(3) Balance the preliminary equation (if necessary), *i.e.*, increase the number of atoms, or molecules, or both, as necessary, until the number of atoms of each element (free or combined) is the same on each side of the equation (§ 110).

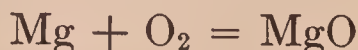
(4) Check the final equation. (See § 110.)

110. Writing equations. — Let us take several examples of the simplest way.

1. Magnesium combines with oxygen to form magnesium oxide.

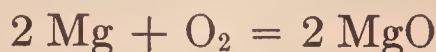
(1) The symbols and formulas are Mg, O₂, and MgO. The last is found (if not remembered) by looking up the name (magnesium oxide) in the Index and referring to the page where this substance is described.

(2) The preliminary equation is : —



(3) Inspection shows 2 atoms of oxygen (in O₂) are on the left and only 1 (in MgO) is on the right. Hence the preliminary equation must be balanced, *i.e.*, we must increase the number of oxygen atoms on the right. We do this by

prefixing the coefficient 2 to the formula MgO , *not by altering the formula* MgO . This change increases the Mg to 2 (because a coefficient multiplies a whole formula) and necessitates multiplying Mg on the left by 2. The balanced equation then becomes: —



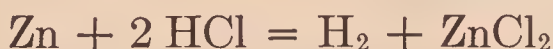
(4) Final checking shows the same number of atoms of each element on both sides of the equation, hence the equation is correct.

2. Zinc and hydrochloric acid form hydrogen and zinc chloride.

(1) and (2) The preliminary equation is: —



(3) Inspection shows 2 atoms of chlorine (in ZnCl_2) are on the right and only 1 is on the left. Hence we must multiply HCl by 2, thereby providing 2 atoms of chlorine, and giving also 2 atoms of hydrogen. The balanced equation becomes: —



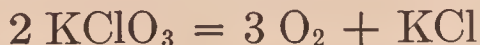
(4) Checking shows this equation is correct.

3. Potassium chlorate decomposes into oxygen and potassium chloride.

(1) and (2) The preliminary equation is: —



(3) Inspection shows 3 atoms of oxygen (in KClO_3) are on the left and only 2 (in O_2) are on the right. So we multiply KClO_3 by 2 and O_2 by 3. The second preliminary equation is: —



Inspecting again, it is obvious there are 2 K and 2 Cl on the left, but only 1 of each is on the right. Therefore, we balance by multiplying KCl by 2, and obtain as a final equation: —



(4) The equation checks, and is, therefore, correct.

111. Some precautions to be observed in writing equations by the above method. — (a) Correct formulas must be used. If a formula is not remembered or is not given in the immediate text, do not guess. Look it up in the book by finding the name of the substance in the Index and consulting the proper page where, as a rule, the formula is given.

(b) It must not be overlooked that the correct formulas of many elementary gases, such as oxygen, hydrogen, nitrogen, and chlorine, are O_2 , H_2 , N_2 , Cl_2 respectively (not O, H, etc.).

(c) Only the substances that actually take part in the chemical change should be included in the equation. Thus, when magnesium is burned in air, the nitrogen of the air does not unite with the magnesium (to any extent). Hence nitrogen does not appear in the equation. Similarly in the equation for the preparation of hydrogen from zinc and hydrochloric acid, no water (H_2O) appears as a factor because the water (in the dilute acid), being only a solvent, does not participate in the reaction. And in the equation for the preparation of oxygen from potassium chlorate and manganese dioxide, the manganese dioxide is omitted because it acts only as a catalyst.

(d) In **balancing an equation** these rules are helpful: —

(1) Start with the formula containing the most atoms of one element.

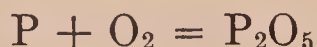
(2) Find the other formula (or symbol) containing this element, and increase the number of atoms of this element by prefixing a coefficient, not by altering the formula (or symbol) — see § 110 1 (3).

(3) Increase again, if necessary.

(4) Balance in the same way for the other elements.

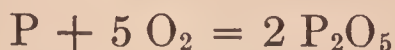
(5) Check up, so that finally the total number of atoms of each element is the same on both sides.

Let us take an example. When phosphorus burns in oxygen, phosphorus pentoxide is formed. The formula of phosphorus pentoxide is P_2O_5 . Hence the preliminary equation is: —

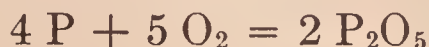


By inspection we see that P_2O_5 needs at least 5 atoms of oxygen. Clearly the only way to balance the equation for

oxygen is to multiply O_2 by 5 and P_2O_5 by 2; this adjustment gives 10 atoms of oxygen on each side, thus: —

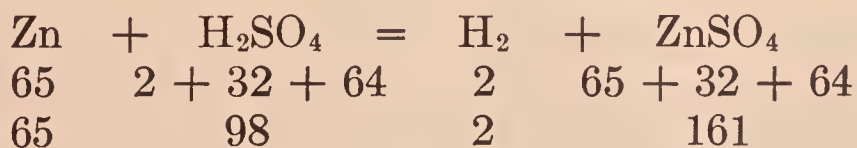


But multiplying P_2O_5 by 2 gives 4 atoms of P on the right, because a coefficient multiplies the whole formula. That is, $2 P_2O_5$ means two molecules each containing 2 P and 5 O. Hence we balance for P by multiplying P on the left by 4. The final equation then becomes: —



112. Calculations from equations. — Equations enable us to find the weights of the substances that can be obtained from (or are needed for) a given weight of a single substance. Knowing one weight, and the proportions by weight in which the whole reaction occurs, we can readily calculate all other weights involved.

Consider the reaction between zinc and sulfuric acid. The complete equation is: —



The equation in this form is read: 65 parts by weight of zinc plus 98 parts by weight of sulfuric acid equal 2 parts by weight of hydrogen and 161 parts by weight of zinc sulfate. That is, these numbers are the relative weights of the different substances involved in this reaction, *viz.*, zinc and sulfuric acid in the ratio of 65 to 98 and hydrogen and zinc sulfate in the ratio of 2 to 161.

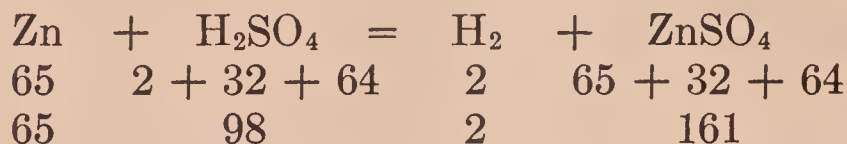
In actual practice we need not start with exactly 65 gm. of zinc or with 98 gm. of sulfuric acid. We can use any convenient weights; but whatever weights we use, these two substances interact in the ratio of 65 to 98 and the quantity of either substance greater than the amount for the required ratio will be left unchanged.

Suppose the problem to be solved is this: What weight of sulfuric acid is needed to interact completely with 45 gm. of zinc? We follow strictly these steps: —

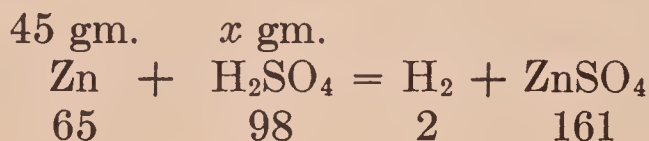
(1) Write the **chemical equation**. Thus: —



(2) Write the **relative weight equation** by placing *under* each symbol and formula the weight for which the complete symbol or formula stands (using the approximate atomic weights in the Table on the inside back cover). Thus: —



(3) Write the **reacting weight equation** by placing the weight given in the problem *above* the proper symbol or formula (45 gm. above Zn in this case) and x gm. above the formula of the required substance (sulfuric acid here). Thus: —



(4) State in a **proportion** the four quantities involved. In this proportion the equation weights (below, in the equation) are the first and second terms, while the corresponding known and required weights (above, in the equation) are the other two terms. Thus: —

$$65 : 98 :: 45 : x$$

(5) **Solve the proportion** for x , remembering that the product of the means (the two inner terms) equals the product of the extremes (the two outer terms). Thus: —

$$98 \times 45 = 65 \times x. \quad \therefore x = \frac{98 \times 45}{65}, \text{ or } 67.8. \quad \text{Ans. } 67.8 \text{ gm.}$$

Instead of steps (3) and (4) an alternative method may be used. Thus, if 65 gm. of zinc require 98 gm. of sulfuric acid, 1 gm. of zinc will require $98 \div 65$, or 1.507, and 45 gm. would require 45×1.507 , or 67.8 gm.

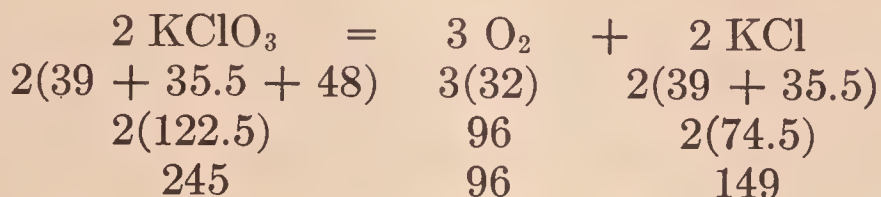
Problems involving volume are readily solved. Let us take two examples.

1. We start with 15 gm. of potassium chlorate and wish to know the volume of oxygen which can be obtained. We find the weight, first, by proceeding as above. Thus:—

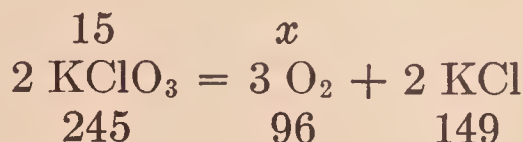
(1) Chemical equation:—



(2) Relative weight equation:—



(3) Reacting weight equation:—



(4) Proportion:—

$$245 : 96 :: 15 : x$$

(5) Solution for weight:—

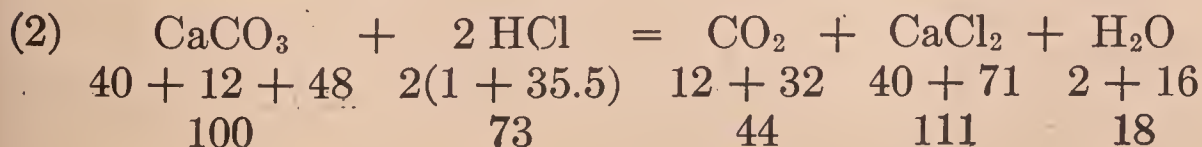
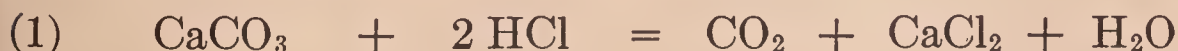
$$96 \times 15 = 245 \times x. \quad \therefore x = \frac{96 \times 15}{245}, \text{ or } 5.87$$

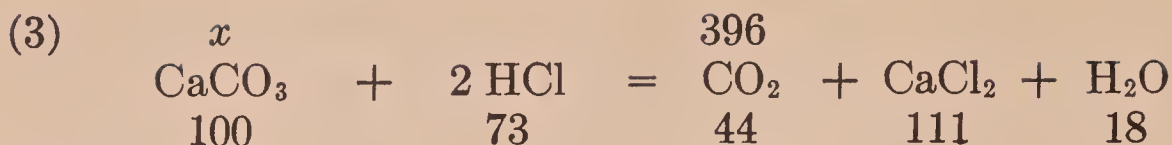
(6) Solution for volume:—

Since 1 liter of oxygen weighs 1.429 gm.,

$$5.87 \div 1.429 = 4.1. \quad \text{Ans. } 4.1 \text{ l.}$$

2. We wish to know the weight of calcium carbonate needed to produce 200 l. of carbon dioxide. First, we find the weight of 200 l. of carbon dioxide. Since 1 l. weighs 1.98 gm., the weight of 200 liters is 200×1.98 , or 396 gm. To find the weight of calcium carbonate needed for 396 gm. of carbon dioxide, we proceed as follows:—





$$(4) \quad 100 : 44 :: x : 396$$

$$(5) \quad 44 \times x = 100 \times 396. \quad \therefore x = \frac{100 \times 396}{44}, \text{ or } 900 \text{ Ans.}$$

Hence in solving problems involving volume we simply find (1) the volume corresponding to the calculated weight or (2) the weight equal to a given volume, and then solve for the required weight.

EXERCISES

1. Write equations for the following reactions: (a) Calcium and hydrochloric acid form calcium chloride and hydrogen. (b) Potassium sulfate and barium chloride form barium sulfate and potassium chloride. (c) Calcium carbonate and hydrochloric acid form calcium chloride, water, and carbon dioxide.

2. As in Exercise 1: (a) Calcium oxide and carbon dioxide form calcium carbonate. (b) Chlorine and aluminum form aluminum trichloride. (c) Carbon and lead oxide (PbO) form lead and carbon monoxide.

3. Balance these equations: (a) $\text{BaCl}_2 + \text{H}_2\text{SO}_4 = \text{BaSO}_4 + \text{HCl}$; (b) $\text{Pb}(\text{NO}_3)_2 + \text{H}_2\text{S} = \text{PbS} + \text{HNO}_3$; (c) $\text{AlCl}_3 + \text{NH}_4\text{OH} = \text{Al}(\text{OH})_3 + \text{NH}_4\text{Cl}$; (d) $\text{NaOH} + \text{CO}_2 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$.

4. Balance these equations: (a) $\text{HCl} + \text{ZnO} = \text{ZnCl}_2 + \text{H}_2\text{O}$; (b) $\text{H}_2\text{SO}_4 + \text{NaNO}_3 = \text{Na}_2\text{SO}_4 + \text{HNO}_3$; (c) $\text{SO}_2 + \text{O}_2 = \text{SO}_3$.

PROBLEMS

(Some of these problems may be used in subsequent assignments.)

1. How many grams of oxygen can be prepared from (a) 45 gm. of mercuric oxide, (b) 1 kg. of potassium chlorate, (c) 1000 gm. of water?

2. As in Problem 1, from (a) 750 gm. of lead dioxide (PbO_2), (b) 2200 gm. of barium dioxide (BaO_2)?

3. Hydrogen is prepared from sulfuric acid and 40 gm. of zinc. Calculate the weights of the products of the reaction.

4. If a balloon holds 150 kg. of hydrogen, how much (a) zinc and (b) sulfuric acid are needed to generate the gas?

5. What volume of oxygen (at 0°C . and 760 mm.) can be obtained from 10 gm. of potassium chlorate?

6. If 10 gm. of pure carbon are burned in air, what weights of other substances are involved?

7. One gm. of copper is heated intensely in air, and the product is reduced by a gas. Calculate (a) the weights of the other substances involved in the two reactions, and (b) the volume of the gas in the second reaction.

8. How many grams of potassium chlorate are needed to prepare (a) 100 gm. of oxygen and (b) 100 l. (at 0° C. and 760 mm.)?

9. Calculate the weights needed in the following reactions: (a) water and 100 mg. of sodium, (b) calcium and 100 mg. of water, (c) sodium hydroxide and 25 gm. of aluminum.

10. What weight of carbon dioxide is formed by burning a ton of coal which is 90 per cent carbon?

11. Suppose 85 gm. of water are decomposed. What (a) weights and (b) volumes of gases are produced?

12. Sixty grams of mercuric oxide are decomposed. What volume of oxygen (at 0° C. and 760 mm.) is produced?

13. How much water can be obtained from (a) 34 gm. of crystallized zinc sulfate ($\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$), (b) 1000 kg. of crystallized calcium sulfate ($\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$), (c) 1000 gm. of washing soda crystals ($\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$)?

14. Write the equation for the interaction of barium nitrate and sodium sulfate. If 170 gm. of barium nitrate are used, calculate the weights of the other compounds involved.

15. Ammonia and hydrogen chloride form solid ammonium chloride. Write the equation for this reaction. If 210 gm. of ammonia are used, calculate (a) the weights of the other compounds involved and (b) the volumes of ammonia and hydrogen chloride needed.

16. The oxygen is liberated from 10 gm. of potassium chlorate, and 10 gm. of sulfur are burned in the gas. How much sulfur, if any, is left?

CHAPTER X

VALENCE

113. What is valence? — Atoms and radicals form molecules. This is merely another way of saying atoms and radicals have a certain chemical property, *viz.*, a capacity to combine and displace. The number which expresses this combining or replacing capacity of an atom or a radical is called its **valence**. Usually we speak of the valence of an element or a radical, *e.g.*, the valence of hydrogen is 1 and of SO_4 is 2, though we mean the combined element or radical. Free or uncombined elements have the valence of zero.

114. Hydrogen is the standard for reckoning valence. — No atom has a combining or replacing capacity lower than a hydrogen atom. Hence the hydrogen atom is the standard and its valence is 1. This means that 1 hydrogen atom holds finally in combination only 1 atom or 1 radical. Thus, in HCl and HNO_3 1 atom of hydrogen is combined with 1 Cl atom and 1 NO_3 radical.

115. Classification of elements and radicals by their valence. — Several elements and radicals have the same combining and replacing capacity as hydrogen, *i.e.*, their atoms and the radicals combine with or displace 1 hydrogen atom. The valence of these elements and radicals is 1, and, like hydrogen, they are called *univalent elements and radicals*, *e.g.*, chlorine, sodium, and the nitrate (NO_3) and hydroxyl (OH) radicals. (See Tables in § 117.)

Many elements and radicals have the combining and replacing capacity of 2 hydrogen atoms, *i.e.*, their valence is 2 and they are called *bivalent elements and radicals*, *e.g.*, oxygen, calcium, and the sulfate radical (SO_4). Similarly,

there are *trivalent elements and radicals*, whose valence is 3, *e.g.*, aluminum and the phosphate radical (PO_4); *quadrivalent*, whose valence is 4, *e.g.*, carbon; *quinquivalent*, whose valence is 5, *e.g.*, phosphorus, and so on up to 8 — the limit.

Atoms and radicals which have the valence 1 are sometimes called *monads*; similarly, we have *dyads*, *triads*, *tetrads*, *pentads*, etc.

116. Positive and negative valence. — There are two kinds of valence — **positive** and **negative** which are designated by the signs $+$ and $-$ respectively. This division corresponds in general to the metallic or non-metallic character of the element. Thus, metals, *e.g.*, sodium and calcium, have a positive valence. Whereas, non-metals, *e.g.*, oxygen and chlorine, have a negative valence. The radical ammonium is positive, whereas the other radicals are negative.

The division according to metals and non-metals is helpful. A better basis for division is the electrical behavior, *e.g.*, in electrolysis, which will be studied in §§ 180–182. There we shall learn that if an element or radical goes to the cathode (negative electrode of the electrolytic apparatus), the valence is positive, but if it goes to the anode (positive electrode), the valence is negative.

On the electrical basis, for example, the valence of combined hydrogen is $+1$, oxygen is -2 , calcium is $+2$, and the SO_4 -radical is -2 . These valences are sometimes written H^{+1} , O^{-2} , Ca^{+2} , SO_4^{-2} .

The usual valence of the common elements and radicals in compounds is shown in the accompanying table. We should always remember that *the valence of a free (i.e., uncombined) element is zero*, *e.g.*, H^0 , 2Cl^0 , N_2^0 . Hence, the valence in the table means that these symbols and formulas have the designated valence *in compounds*, *e.g.*, free hydrogen is H^0 but combined hydrogen is H^{+1} , and (by analogy) free OH is OH^0 but OH in NaOH is OH^{-1} .

117. Tables of valence. — The usual valence of the common elements and radicals is shown in Table III, A and B. These tables are very useful in writing formulas (§ 118).

TABLE III. — A. POSITIVE VALENCE OF ELEMENTS AND RADICALS

NAME	SYMBOL	POSITIVE VALENCE	NAME	SYMBOL	POSITIVE VALENCE
Aluminum	Al	+ 3	Lead	Pb	+ 2
Ammonium	NH ₄	+ 1	Magnesium	Mg	+ 2
Barium	Ba	+ 2	Mercury (ous)	Hg	+ 1
Calcium	Ca	+ 2	Mercury (ic)	Hg	+ 2
Carbon	C	+ 4	Phosphorus (ic)	P	+ 5
Copper (ic)	Cu	+ 2	Potassium	K	+ 1
Gold (ic)	Au	+ 3	Silicon	Si	+ 4
Hydrogen	H	+ 1	Silver	Ag	+ 1
Iron (ous)	Fe	+ 2	Sodium	Na	+ 1
Iron (ic)	Fe	+ 3	Zinc	Zn	+ 2

TABLE III. — B. NEGATIVE VALENCE OF ELEMENTS AND RADICALS

NAME	SYMBOL OR FORMULA	VALENCE	NAME	SYMBOL OR FORMULA	VALENCE
Bromine	Br	— 1	Iodine	I	— 1
Carbonate	CO ₃	— 2	Nitrate	NO ₃	— 1
Chlorate	ClO ₃	— 1	Oxygen	O	— 2
Chlorine	Cl	— 1	Permanganate	MnO ₄	— 1
Dichromate	Cr ₂ O ₇	— 2	Phosphate	PO ₄	— 3
Ferrocyanide	Fe (CN) ₆	— 4	Sulfate	SO ₄	— 2
Hydroxide	OH	— 1	Sulfate (acid)	HSO ₄	— 1

Some elements have more than one valence because they form different kinds of compounds. Thus, the valence of iron is + 2 in ferrous compounds and + 3 in ferric compounds, *e.g.*, ferrous sulfate, Fe⁺²SO₄⁻² and ferric chloride Fe⁺³Cl₃⁻¹⁻¹⁻¹. Similarly, sulfur is S⁺² in sulfides, S⁺⁴ in sulfur dioxide, and S⁺⁶ in sulfur trioxide. In general, the valence in Tables A and B is the numerical value in common compounds, particularly compounds of two elements or

of an element and a radical, *e.g.*, $\text{Na}^{+1}\text{Cl}^{-1}$, $\text{Ca}^{+2}\text{SO}_4^{-2}$, $\text{Cu}^{+2}(\text{NO}_3)_2^{-1-1}$.

118. Writing formulas by positive and negative valence. — The formulas of many compounds can be written by utilizing two rules: —

1. Atoms and radicals of the opposite kind of valence combine, *i.e.*, positive with negative.

2. The positive and the negative parts must be numerically equal, *i.e.*, the valence must balance and the algebraic sum must be 0.

Let us take some examples.

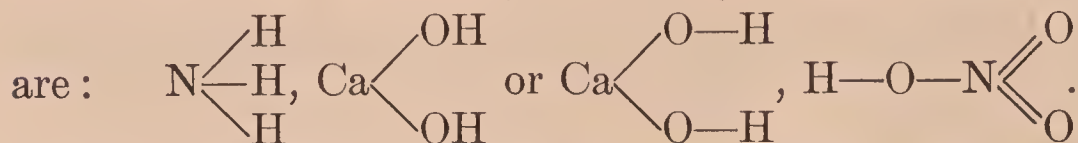
(a) What is the formula of calcium sulfate? From Table A calcium is + 2, and from Table B the sulfate radical is - 2. Hence the formula is $\text{Ca}^{+2}\text{SO}_4^{-2}$, or CaSO_4 .

(b) What is the formula of aluminum oxide? From Table A aluminum is + 3 and from Table B oxygen is - 2. To make the parts balance, we need $2 \times (+3) = +6$ and $3 \times (-2) = -6$, or 2 Al and 3 O; hence we write $\text{Al}_2^{+3+3}\text{O}_3^{+2+2+2}$ or Al_2O_3 .

(c) How are formulas of salts derived? Formulas of salts are frequently needed. These can be readily written by learning the formulas of the common acids and substituting the correct number of atoms for the hydrogen. Thus, the formula of sulfuric acid is H_2SO_4 . Therefore, all sulfates will have one or more SO_4 -radicals as one part of the formula and one or more atoms of a metal for the other part. If the metal has the valence of + 1, the formula will contain two atoms of the metal, *e.g.*, Na_2SO_4 ; if the valence of the metal is + 2, there will be only one atom, *e.g.*, CuSO_4 . Whereas if the valence is + 3, there will be two atoms of the metal and three SO_4 -radicals, *e.g.*, $\text{Al}_2(\text{SO}_4)_3$. Similarly, all nitrates have NO_3 (one or more), all chlorides have Cl (one or more), all phosphates have PO_4 (one or more).

119. Representation of valence. — The valence of elements and radicals may be represented in various ways. One has already been given (exponent with proper sign), *e.g.*, H^{+1} , SO_4^{-2} . Sometimes short lines are used, *e.g.*, $\text{H}-$, $\text{O}==$, $-\text{O}-$, $\text{Al}\equiv$, etc. If lines are used to represent valence in compounds, a single line answers for two elements.

Thus, the formula of water is written H—O—H . Similarly, the formulas of ammonia, calcium hydroxide, and nitric acid



Such formulas are called **structural or graphic formulas**, for they show the probable arrangement of the atoms in the molecules. It must not be forgotten that structural formulas are merely representations; the lines are intended to indicate the numerical value of the valence and not the strength of the combination of the atoms.

EXERCISES

(Some of these Exercises may be used in subsequent assignments.)

1. What is the valence of: (a) H, O, C, Cl; (b) Ag, K, Na, NH_4 ; (c) NO_3 , OH; (d) Ba, Ca, Cu, Fe (ous), Mg, Pb, Zn; (e) CO_3 , SO_4 , S (ide); (f) Al, Fe (ic), PO_4 ?

2. State the fundamental rules for writing formulas from valence.

3. Write the formula of the chloride of potassium, sodium, silver, copper, mercury (ous), mercury (ic), iron (ous), iron (ic), zinc, calcium, barium, magnesium, aluminum, ammonium, lead.

4. Write the formula of the sulfate of K, Na, Ag, Cu, Fe (ous), Zn, Pb, Ca, Ba, Mg, Al, NH_4 .

5. Write the formula of the following compounds and indicate the valence of each element or radical: ammonium chloride, potassium carbonate, barium phosphate, zinc iodide, ammonium dichromate, silver sulfate, magnesium oxide, sodium dichromate, aluminum chloride, ferrous bromide, calcium phosphate, mercurous nitrate.

6. Write the formulas of the following (as in Exercise 5): ferrous carbonate, aluminum phosphate, calcium iodide, sodium permanganate, phosphoric acid, carbonic acid.

7. Write the formula of the nitrate of calcium, silver, iron (ic), mercury (ous), barium, magnesium, aluminum.

8. Write the formula of the oxide of Al, Ba, Ca, Na, Ag, K, Zn, Mg.

9. Write the formula of (a) the carbonate of Cu, Ba, Ag; (b) the iodide of Hg (ous and ic), Pb, Ag, Na, Fe (ous and ic), Al; (c) the chlorate of Na, Ba, Ag.

10. Write the formula of (a) the dichromate of Pb, Na, Al, Ag; (b) the phosphate of Na, Ca, Ag; (c) the nitrate of Pb, Ca, Cu.

PROBLEMS

See Problems at the end of Chapters VIII and IX.

CHAPTER XI

CHLORINE — HYDROGEN CHLORIDE — HYDROCHLORIC ACID

120. Occurrence of chlorine. — Free chlorine is never found in nature because it is such an active chemical element. But some of its compounds, especially chlorides, are widely distributed. The most abundant compound is sodium chloride (NaCl) or common salt. Thick beds of compounds of chlorine with potassium, magnesium, and calcium occur in the Stassfurt region in Germany and the Alsace-Lorraine district in France; some beds are almost entirely potassium chloride. Ocean water and the water of such lakes as the Dead Sea and the Great Salt Lake contain a large proportion of sodium chloride.

121. Manufacture of chlorine.

— Chlorine is manufactured by the **electrolysis** of a solution of sodium chloride (Figs. 49, 50).

When an electric current is passed through a solution of sodium chloride, chlorine is liberated in one compartment of the apparatus and sodium hydroxide is formed in the other. The chlorine gas is usually conducted off through a pipe (*A* in Fig. 49) and compressed to a liquid in strong metal tanks (Fig. 52).

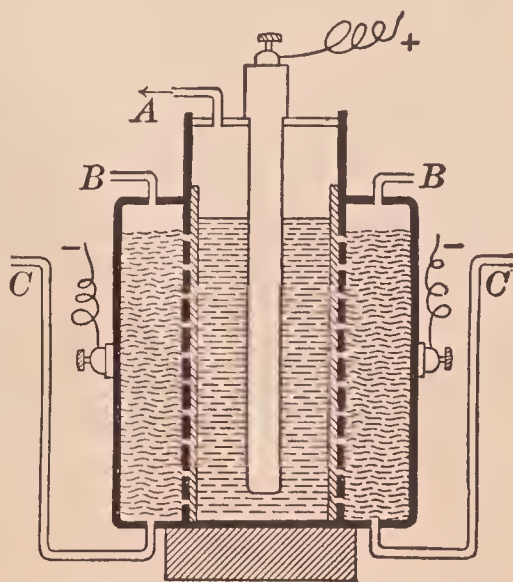


FIG. 49. — Vertical sketch of one form of apparatus for manufacturing chlorine by the electrolysis of a solution of sodium chloride. The chlorine escapes through the pipe *A*.

The sodium hydroxide dissolves and the solution is drawn off at intervals. This process is more fully described in § 285.

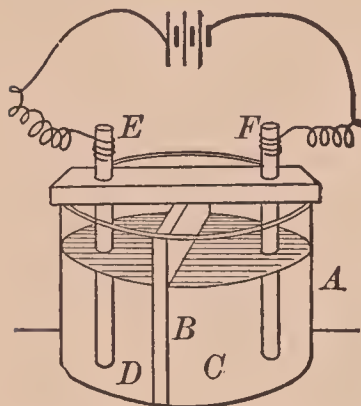
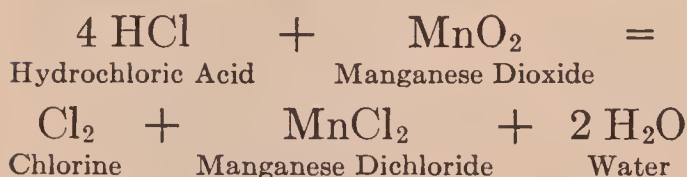


FIG. 50. — Laboratory apparatus for the preparation of chlorine by the electrolysis of a solution of sodium chloride.

The manufacture of chlorine can be readily demonstrated in the laboratory. The apparatus is shown in Fig. 50. A solution of sodium chloride is put in the battery jar *A*; a little litmus solution is added and then enough dilute hydrochloric acid to color the solution a distinct red. A block *B* divides the jar into two compartments *C* and *D*, and the two pieces of electric light carbon serve as electrodes *E* and *F*. Soon after the current (from a storage battery or four or more dry cells) is turned on, the solution is bleached by the liberated chlorine in one compartment and turned blue by the sodium hydroxide in the other. The chlorine can also be detected by its choking odor.

122. Preparation of chlorine in the laboratory. — Chlorine is prepared in the laboratory by heating concentrated hydrochloric acid with an oxidizing agent, such as potassium permanganate (KMnO_4) or manganese dioxide (MnO_2). The equation for the reaction with manganese dioxide is: —



If only a small quantity of chlorine is wanted, enough crystallized potassium permanganate is put into a warm bottle to form a thin layer, 5 cc. of concentrated hydrochloric acid is added, and the bottle is covered with a piece of filter paper. Chlorine (gas) soon fills the bottle. If a larger quantity is needed, the apparatus shown in Fig. 51 may be used.

Manganese dioxide is put into the flask *A* and concentrated hydrochloric acid is introduced through the dropping tube *B*.

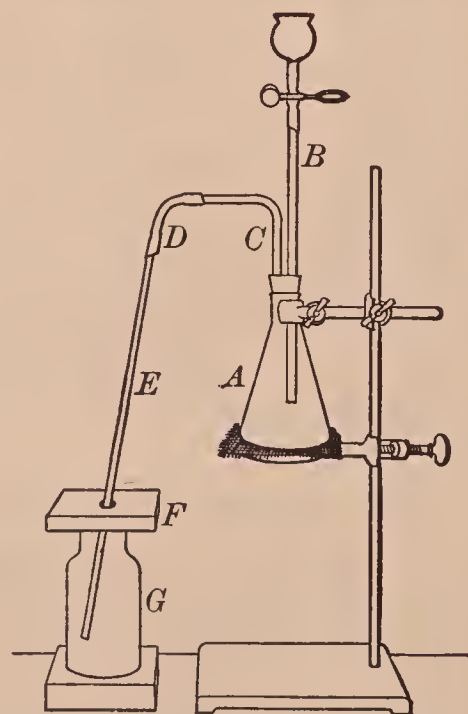


FIG. 51. — Apparatus for preparing chlorine in the laboratory from hydrochloric acid and manganese dioxide.

By heating the flask gently,

chlorine passes to the bottom of the bottle *G*, rises slowly, and displaces the air.

123. Physical properties of chlorine. — Chlorine is a greenish yellow gas. It has a stifling odor. If breathed, it irritates the lining of the nose and throat; a large quantity produces suffocation, and would ultimately cause death. Chlorine was the first poison gas used in the World War. When chlorine is used in manufacturing or purifying plants, a gas mask is usually worn (Fig. 52).

Chlorine is a heavy gas — about 2.5 times heavier than air. A liter at 0° C. and 760 mm. weighs 3.22 gm.

Chlorine can be readily liquefied. Liquid chlorine is sold in strong metal cylinders (Fig. 52 and also Fig. 53).

Chlorine dissolves in water. The solution is yellowish, and smells like chlorine. **Chlorine water**, as the solution is called, is unstable. If the solution is placed in the sunlight, oxygen is slowly liberated and can be collected in a suitable apparatus (Fig. 45, § 96).

The oxygen does not come directly from the water but from a compound of chlorine called hypochlorous acid (HClO), which is formed in small quantities in the solution; some hydrochloric acid is also formed. The reaction may be represented thus:—

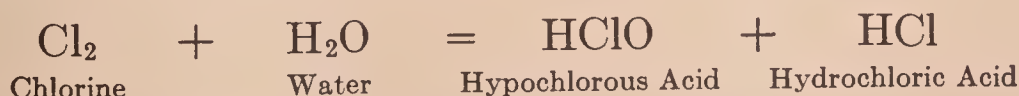
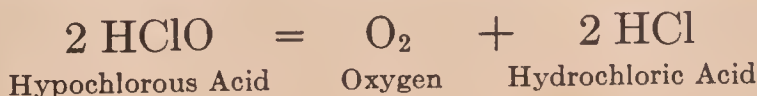
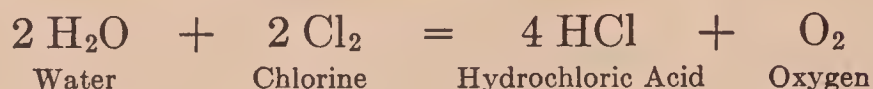


FIG. 52. — Workman protected by a gas mask while repairing a leak in a tank of liquid chlorine.

The hypochlorous acid is unstable and decomposes, thus:—



The reactions continue until all the chlorine is used up; so the equation for the completed change is: —



124. Chemical properties of chlorine. — Chlorine combines vigorously with many elements and interacts with many compounds. And just as oxygen — another active element — forms oxides, so chlorine forms chlorides.

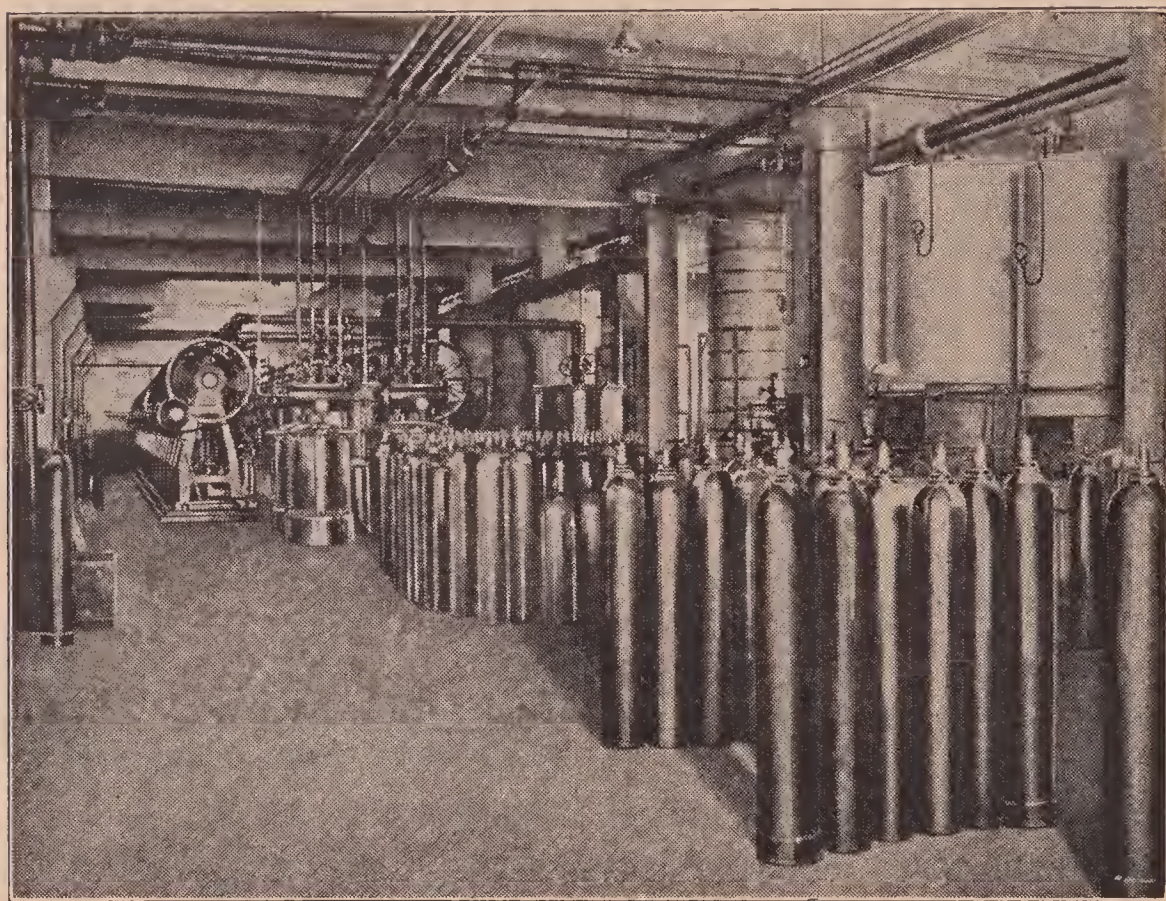


FIG. 53. — Interior of a plant for liquefying and storing chlorine. Cylinders full of chlorine are in the foreground.

The uniting of chlorine with elements is easily shown. Thus, if sodium, iron, copper, or other metals are slightly warmed and put into chlorine, they unite with the chlorine at once; the sodium produces a dazzling light, and the copper and iron glow and emit dense fumes. These chemical changes illustrate the broad use of the term *combustion*. No oxygen is involved. Chlorine and the metal unite, and the chemical change is attended with heat and light. The

compound formed in each case is a **chloride**, *i.e.*, a compound of chlorine and one other element. Thus, sodium and iron form sodium chloride (NaCl) and iron chloride (FeCl_3) respectively.

Chlorine combines readily with hydrogen. A jet of burning hydrogen when lowered into chlorine continues to burn, just as it does in oxygen. The product is a colorless gas called **hydrogen chloride**, which becomes a white cloud in moist air or when the breath (containing moisture) is blown across the mouth of the vessel (§ 131, second paragraph).

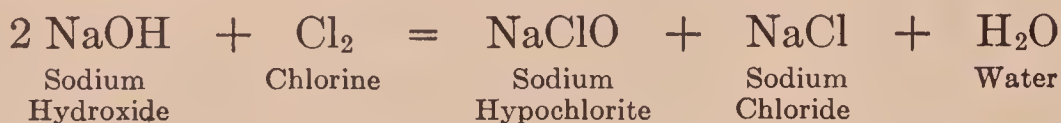
The activity of chlorine toward hydrogen is so great that chlorine withdraws hydrogen chemically from many compounds, *e.g.*, turpentine ($\text{C}_{10}\text{H}_{16}$). Thus, when cotton saturated with hot turpentine is put into chlorine, white fumes, due to the formation of hydrogen chloride, appear at once. Soon the chemical change is so vigorous that a flame is suddenly produced and the white fumes of hydrogen chloride are obscured by a dense cloud of black smoke, which consists of fine particles of carbon (left over from the decomposed turpentine).

125. Chlorine compounds are used for bleaching. — Moist chlorine (essentially hypochlorous acid — § 126) and some chlorine compounds change many colored substances into colorless or pale ones. Thus, for a century or more cloth made of cotton or linen, naturally colored a faint yellow by impure substances, has been bleached (*i.e.*, whitened) by exposure to a moist compound of chlorine called bleaching powder.

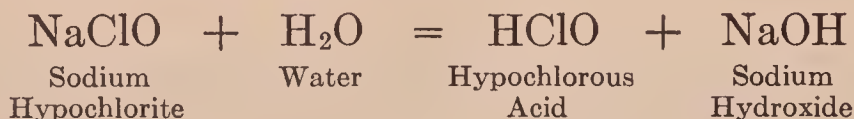
For certain industries, *e.g.*, bleaching cotton cloth, the best bleaching agent is **bleaching powder** (CaOCl_2 or preferably $\text{CaCl}(\text{OCl})$) or, as it is often called, **chloride of lime**. It is a yellowish white substance which smells like chlorine, though the smell is really due to chlorine compounds, which are slowly liberated from the bleaching powder by the moist carbon dioxide in the air.

In using bleaching powder, rather dilute sulfuric acid is mixed with a weak solution (or suspension) of the powder. Hypochlorous acid (HClO) is liberated slowly. This unstable acid yields oxygen, which does the bleaching.

Another compound of chlorine used in bleaching is **sodium hypochlorite** (NaClO). This compound is prepared by passing an electric current through sodium chloride solution and allowing the products to react, thus:—



Sodium hypochlorite is unstable, and a cold dilute solution contains hypochlorous acid, thus:—



The hypochlorous acid, as just stated, decomposes and furnishes the oxygen. Sodium hypochlorite solution is used in bleaching wood pulp and for whitening linen in laundries.

126. The process of bleaching.—The fibers of cotton and linen and also of the pulp obtained from wood consist

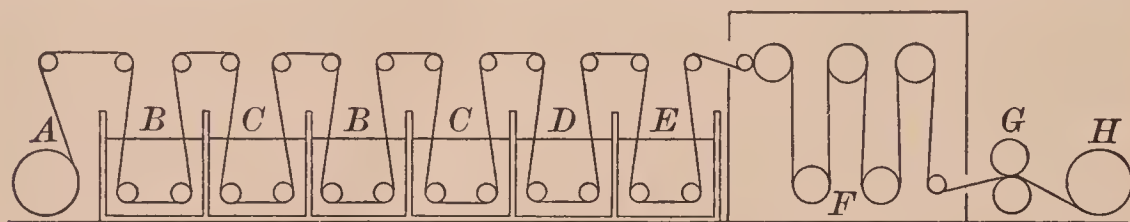


FIG. 54. — Diagram of the process of bleaching cotton cloth.

mainly of cellulose, which is not appreciably affected by dilute hypochlorous acid solutions. But the natural coloring matter in these fibers is slowly oxidized to colorless compounds. Artificial coloring matter, *e.g.*, dye, is usually decomposed (and decolorized) by hypochlorous acid. Some colored fabrics, *e.g.*, those dyed with a mordant (§ 510), are not whitened completely, but only faded, by bleaching. Some dyes, *e.g.*, those used for postage stamps, resist the bleaching action of chlorine compounds. Substances made up largely of carbon cannot be bleached, *e.g.*, printer's ink, "lead" of lead pencils, many canceling inks, and tarry mixtures from coal and petroleum.

A diagram of the process of bleaching cotton cloth is shown in Fig. 54. The pieces are sewed together end to end in long strips and drawn by machinery from the roll A successively through vats contain-
bleach-

ing powder solution *B*, weak acid *C*, and water *D*. At some point toward the end of the process the cloth passes through a vat containing acid sodium sulfite solution (or similar mixture) *E*, called the antichlor, to remove traces of hypochlorous acid. After thorough washing, the cloth is dried and ironed by passing over hot cylinders *F*, *G*, and finally wound on the roll *H*.

127. Uses of chlorine — Besides the use of chlorine in the manufacture of bleaching powder and bleaching mixtures, large quantities are made into useful compounds of chlorine. One is carbon tetrachloride (CCl_4), which is used in “pyrene” fire extinguishers (Fig. 55) because it readily forms a heavy non-combustible vapor which smothers the fire, especially burning gasolene. Carbon tetrachloride is also used as a solvent for extracting greases. The non-combustible cleaning mixture called “carbona” contains carbon tetrachloride. Considerable chlorine is used to purify drinking water, and its use is increasing because it is a convenient and effective way to destroy bacteria (§ 81, Fig. 37).



FIG. 55. — Fire extinguisher containing carbon tetrachloride.

128. Chlorine in the World War. — Chlorine and its compounds played a significant part in the World War. Chlorine and phosgene (COCl_2) were the first poison substances used. Tanks of **liquid chlorine**, or chlorine and **phosgene**, were opened, the gas rushed out, and under favorable conditions was blown along the surface as a great cloud. Because it is heavier than air it sank into the trenches and immediately drove out the men.

The cloud method was soon abandoned for the **shell method**, *i.e.*, gases were replaced by readily volatilized substances, over half being chlorine compounds. In fact chlorine was utilized, directly or indirectly, in preparing about 95 per cent of the toxic substances used to rout out the enemy. Some substances, *e.g.*, chlorpicrin and benzyl chloride, caused a copious flow of tears (“tear gases”). Others, *e.g.*, diphenylchlor-arsine, produced excessive sneezing (“sneeze gases”). Still others, *e.g.*, mustard gas or di-chlor-ethyl-sulfide, irritated the skin and led to serious results.

The effects of these substances were prevented or lessened by gas masks. The masks fitted the face closely, necessitating breathing through a canister. The canister contained a suitable absorbent, usually a dense variety of charcoal, prepared from cocoanut shells and fruit pits,

together with other substances, especially potassium permanganate and soda-lime (a special mixture of lime and sodium hydroxide). The soda-lime reacted with chlorine and chlorine compounds.

Silicon tetrachloride (SiCl_4) mixed with ammonia and water was used as a **smoke screen**, because these three reacted and formed a dense white cloud consisting of fine particles of ammonium chloride (NH_4Cl) and silicic acid (H_4SiO_4). This smoke settled down slowly and screened a vessel or the land (Fig. 56).

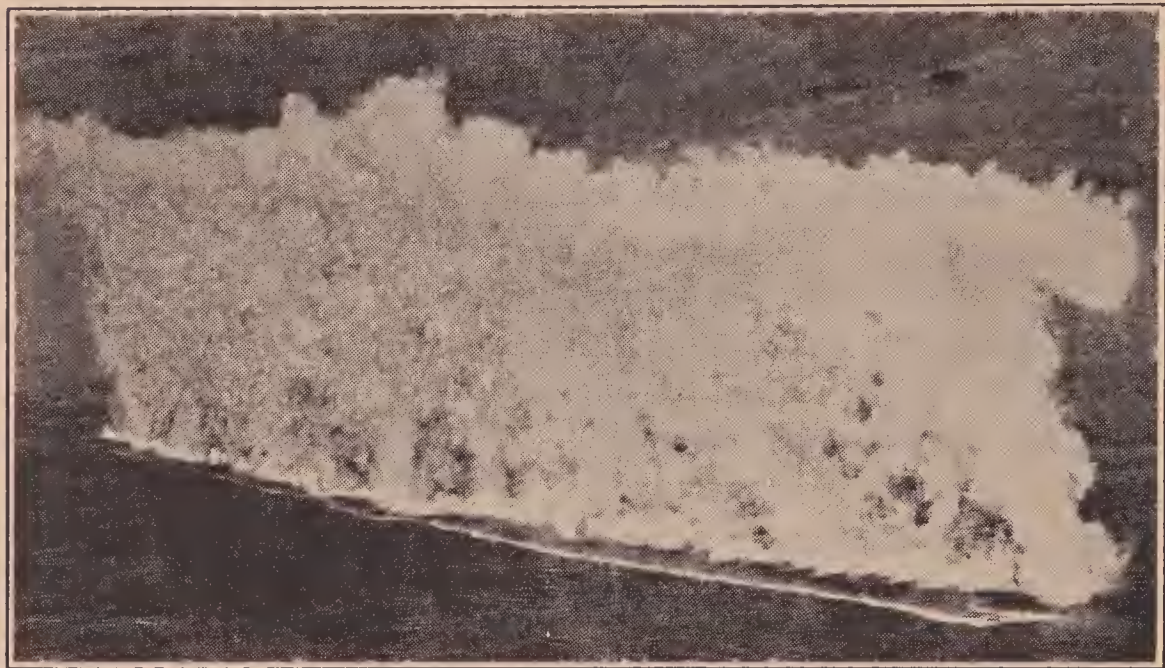
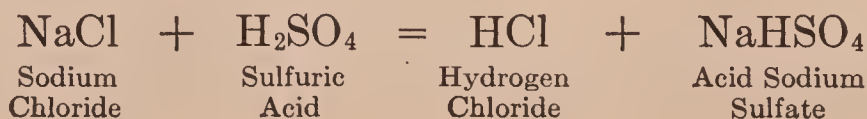


FIG. 56. — A smoke screen laid by a warship off Cape Hatteras.

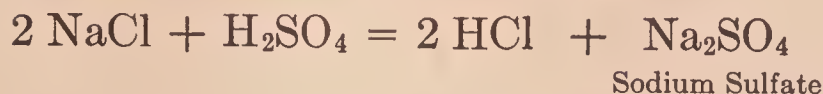
HYDROGEN CHLORIDE AND HYDROCHLORIC ACID

129. Hydrogen chloride and hydrochloric acid. — Hydrogen chloride is a gas, which is very soluble in water. Hydrochloric acid is the common name of a water solution of hydrogen chloride. This solution is known commercially as muriatic acid (from the Latin word *muria*, meaning brine), but it is more properly called hydrochloric acid. Hydrogen chloride is often called hydrochloric acid gas.

130. Preparation of hydrogen chloride. — This gas is prepared in the laboratory by heating sodium chloride with sulfuric acid. If the mixture is heated gently, the chemical change is represented thus: —



But at a high temperature the equation is:—



The gas is collected by passing it to the bottom of a bottle. The solution is prepared by absorbing the gas in water.

Hydrochloric acid is manufactured in enormous quantities by a method essentially like that used in the laboratory.

The mixture of salt and sulfuric acid is heated in a cast iron retort *A* (Fig. 57) by the furnace *B* to a moderate temper-

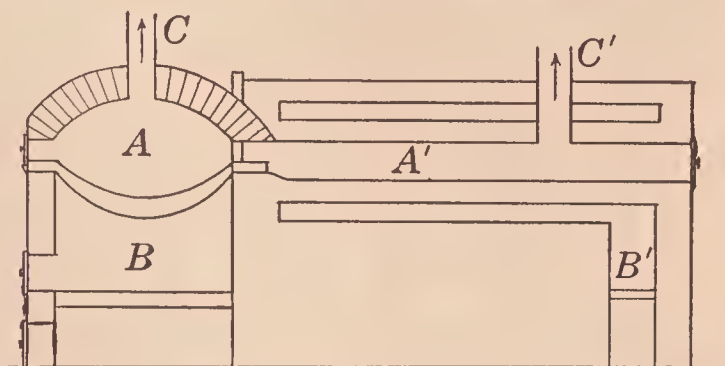


FIG. 57. — Sketch of the furnace used for the manufacture of hydrochloric acid.

ature; as soon as the mass becomes pasty it is raked out upon the flat heater *A'* and heated to a high temperature by the furnace *B'*. The hydrogen chloride passes up through *C* and *C'* into an absorbing system (Fig. 58). It is cooled in the tower *D*, washed, cooled, and absorbed in the tower *E*, absorbed in the stoneware jugs *FFF* (through which weak acid from the absorbing tower flows), and finally absorbed in the tower *G*. The final portion is caught in the jug *H*. The concentrated solution is drawn off at *I*.

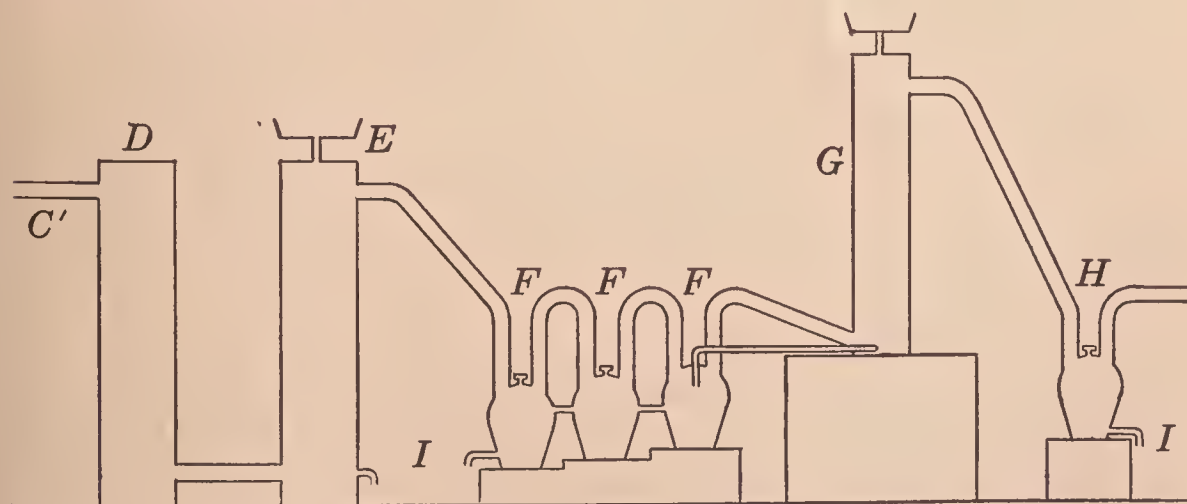


FIG. 58. — Sketch of the absorbing system used for the manufacture of hydrochloric acid.

131. Physical properties of hydrogen chloride.—Hydrogen chloride is a colorless gas. It has a choking, sharp taste, and irritates the lining of the nose and throat. It is

about 1.25 times heavier than air. A liter at 0°C . and 760 mm. weighs 1.64 gm.

The solubility of hydrogen chloride in water is one of its most striking properties. When it escapes into moist air, it forms white fumes which are really minute drops of a solution of the gas in the moisture of the air.

The solubility of hydrogen chloride in water can be shown by a simple experiment (Fig. 59). The flask *A* is filled with hydrogen chloride.

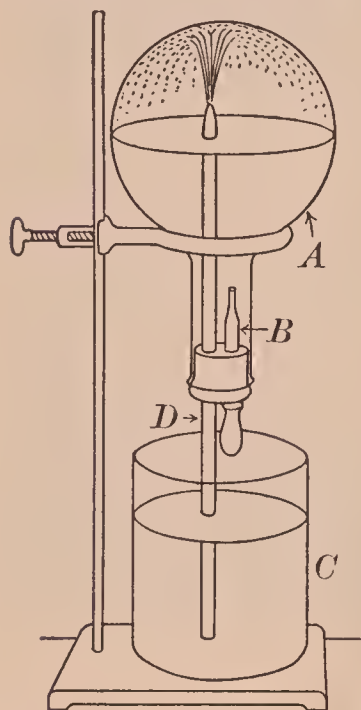


FIG. 59. — Experiment to illustrate the marked solubility of hydrogen chloride.

The medicine dropper *B* is partly filled with water, the stopper with its tubes is inserted, and the flask is then arranged as shown in the figure. By pinching the bulb of the dropper, a few drops of water are forced into the flask. This small quantity of water dissolves so much gas that a partial vacuum is formed in the flask; pressure within the flask is reduced so much that the atmospheric pressure forces water from the jar *C* up the tube *D* and through the small opening into the flask.

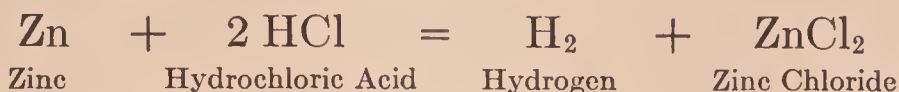
132. Chemical properties of hydrogen chloride. — Hydrogen chloride does not burn nor support combustion. It is a very stable compound and can be heated to about 1800°C . before it begins to decompose. The moist gas unites readily with certain substances, *e.g.*, ammonia; in this case dense white clouds of ammonium chloride (NH_4Cl)

are formed. This reaction is used as a **test for hydrogen chloride**.

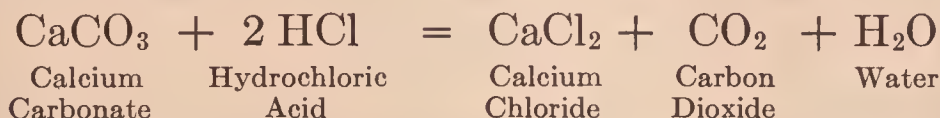
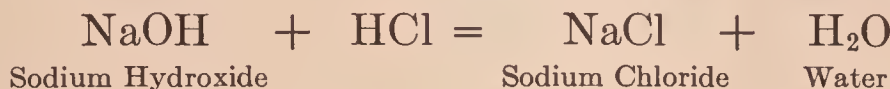
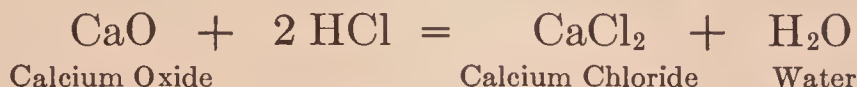
133. Hydrochloric acid. — As previously stated, the water solution of hydrogen chloride is the common substance **hydrochloric acid**, which is sometimes called muriatic acid. The commercial concentrated acid contains about 35 per cent (by weight) of the actual substance HCl . Its specific gravity is about 1.2. The concentrated acid forms white fumes in the air, especially on a moist day, owing to the escape of hydrogen chloride (§ 131, second paragraph).

Hydrochloric acid is a typical acid. It has a sour taste, reddens blue litmus, conducts electricity, and reacts with

most metals, forming hydrogen and salts. The salts are **chlorides** of the metals, *e.g.*, —

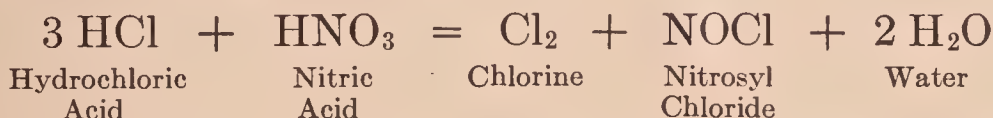


Hydrochloric acid also forms chlorides by interaction with (metallic) oxides, hydroxides, and also with carbonates, thus: —



134. Uses of hydrochloric acid. — Hydrochloric acid is an indispensable compound, and is used frequently in the laboratory and in many industrial processes. Like other acids, it is sold in bottles holding 2.5 liters and in securely packed glass carboys containing 10 or more gallons (Fig. 60).

135. Aqua regia. — Hydrochloric acid and nitric acid interact and liberate chlorine, thus: —



A mixture of three volumes of concentrated hydrochloric acid and one volume of concentrated nitric acid is usually used. If such a mixture is added to a metal which is not affected by either acid alone, the free chlorine together with the hydrochloric acid converts the metal into a soluble compound. Thus, the resistant metal gold forms chlorauric acid (HAuCl_4), which on heating yields soluble gold chloride (AuCl_3).

The alchemists named this mixture of hydrochloric and nitric acids **aqua regia**, meaning “royal water,” to emphasize the fact that it

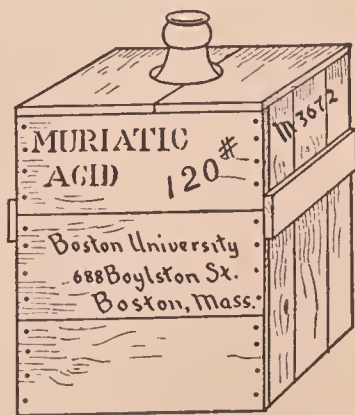
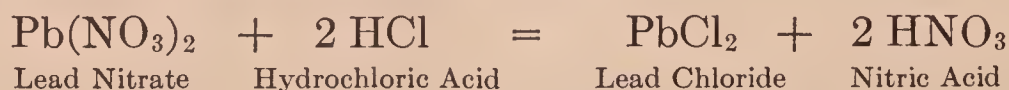


FIG. 60. — A carboy of hydrochloric acid packed for shipment.

dissolves the "noble" metal gold. Another name is nitrohydrochloric acid.

136. Chlorides. — A chloride is a compound of chlorine with another element. Chlorides are formed, as we have already seen, by the direct combination of chlorine and metals (§ 124) and by the interaction of hydrochloric acid with metals, oxides, hydroxides, and carbonates (§ 133).

Most chlorides are soluble in water. But the chlorides of lead (PbCl_2), silver (AgCl), and one of the chlorides of mercury (HgCl) are not soluble. They are formed as insoluble solids, when hydrochloric acid, or a soluble chloride, is added to a solution of a lead compound, silver compound, or the proper mercury compound, *e.g.*, —



The formation of insoluble solids by double decomposition (and certain other changes) is called **precipitation**, and the solid itself is called a **precipitate**. Precipitates often have properties which can be readily observed or determined. Thus, silver chloride is white and curdy, and soon turns purple in the light; it dissolves in ammonium hydroxide, owing to the formation of a complex soluble compound, which, however, is readily transformed by dilute nitric acid back into silver chloride. Other chlorides have different properties. Hence, the precipitation and behavior of silver chloride serve as a **test for hydrochloric acid and soluble chlorides**.

137. Names of chlorides. — A molecule of a chloride may contain one or more atoms of chlorine and in some cases the name of the compound indicates this fact, *e.g.*, manganese dichloride (MnCl_2), antimony trichloride (SbCl_3), carbon tetrachloride (CCl_4). Some metals form two chlorides. Then the two are distinguished by modifying the name of the metal; the one containing the smaller proportion of chlorine ends in *-ous*, that containing the larger in *-ic*. Thus, mercurous chloride is HgCl , and mercuric chloride is HgCl_2 .

EXERCISES

1. How can chlorine be quickly distinguished from other gases?
2. Summarize the chemical properties of chlorine.
3. What is (a) muriatic acid, (b) chloride of lime, (c) bleaching powder, (d) carbon tetrachloride, (e) aqua regia?
4. Write the equation for (a) preparation of chlorine, (b) interaction of chlorine and water, (c) decomposition of hypochlorous acid, (d) preparation of hydrogen chloride, (e) interaction of hydrogen chloride and ammonia, (f) interaction of sodium chloride and silver nitrate.
5. Complete and balance these equations: (a) $\text{NaCl} + \text{H}_2\text{SO}_4 = \text{---} + \text{Na}_2\text{SO}_4$; (b) $\text{H}_2 + \text{---} = \text{HCl}$; (c) $\text{HCl} + \text{Na}_2\text{CO}_3 = \text{---} + \text{CO}_2 + \text{---}$; (d) $\text{HgNO}_3 + \text{---} = \text{HgCl} + \text{HNO}_3$.

PROBLEMS

1. Calculate the weight of chlorine in (a) 2 kg. of sodium chloride, (b) 2 mg. of calcium chloride, (c) 1 gm. of aluminum chloride.
2. How many grams of each product are formed when hydrochloric acid interacts with 85 gm. of manganese dioxide?
3. How many grams of hydrogen chloride can be obtained from 27 gm. of sodium chloride?
4. Calculate the percentage composition of (a) KCl, (b) CaCl_2 .
5. How much sodium chloride can be formed by burning sodium in 40 gm. of chlorine?
6. Calculate the simplest formula of the compound having the composition (a) Hg = 84.92 per cent, Cl = 15.07; (b) Hg = 73.8, Cl = 26.2, (c) N = 26.17, H = 7.48, Cl = 66.35.

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

- Exercise *23 — Preparation and Properties of Chlorine.
Exercise S19 — Preparation and Properties of Chlorine — T.
Exercise S20 — Chlorine Water — T.
Exercise S21 — Bleaching with Bleaching Powder — T.
Exercise *24 — Hydrogen Chlorine and Hydrochloric Acid.
Exercise S22 — Hydrogen Chloride.
Exercise *25 — Tests for Hydrochloric Acid and Chlorides.
Exercise *26 — Insoluble Chlorides.
Exercise S23 — Aqua Regia — T.
Exercise S24 — Types of Chemical Change — T.

SUPPLEMENTARY SECTIONS FROM PART II

The following sections may be selected from Topic XI: —

- 363. Gay-Lussac's law of gas volumes.
- 364. Avogadro's law.
- 365. How Avogadro's law is used to find molecular weights.
- 366. Why the molecular weight of oxygen is 32.
- 367. Finding molecular weights by the vapor density method.
- 368. A molecule of oxygen contains 2 atoms.
- 369. Molecules of other elementary gases contain two atoms.
- 370. A mole.
- 371. How molecular weight is calculated by the molar method.
- 372. Molecular formulas of compounds.
- 373. Molecular formulas of elements.
- 374. Molecular (volumetric) equations.

CHAPTER XII

NITROGEN — THE AIR — ARGON AND HELIUM — LIQUID AIR

138. Introduction. — The atmosphere is the gas that envelops the earth. It extends several miles into space. The terms *atmosphere*, *the air*, and *air* are often used interchangeably; though by *the air* or *air* we usually mean a limited portion of the atmosphere, *e.g.*, the air of a room.

139. Occurrence of nitrogen. — The gas nitrogen comprises about four-fifths by volume (§ 145) of the air. There are many compounds of nitrogen, *e.g.*, nitric acid (HNO_3), sodium nitrate (NaNO_3), and ammonia (NH_3). Nitrogen is also a constituent of many animal and vegetable substances, *e.g.*, the proteins, which are indispensable ingredients of our food and also of the muscles and nerves of our bodies.

140. Preparation of nitrogen. — Nitrogen is prepared on an industrial scale from liquid air (§§ 155, 156). When liquid air is allowed to evaporate slowly, the nitrogen escapes first and is collected in a separate tank.

Nitrogen can also be obtained from air by removing the oxygen, *e.g.*, industrially from producer gas (§ 65) and in the laboratory by phosphorus (Fig. 61).

Phosphorus is put in a small dish or a crucible cover supported on a cork floating in a vessel of water. Upon igniting the phosphorus (**Care!**) with a hot wire and placing a bell jar quickly over the cork, the phosphorus and oxygen unite, forming clouds of white phosphorus pentoxide

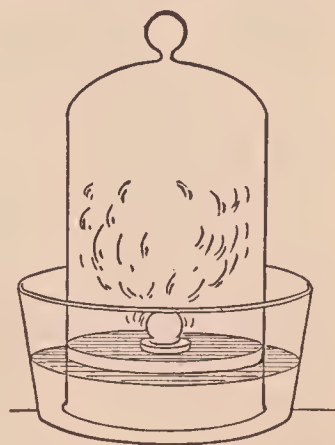
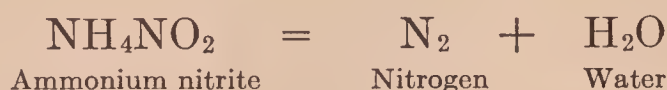


FIG. 61. — Preparation of nitrogen from air by burning out the oxygen with phosphorus.

(P_2O_5). This solid soon dissolves in the water, which rises inside the jar owing to the removal of the oxygen, and the nitrogen is finally left. CAUTION: This experiment is dangerous and great care must be used.

The most convenient way to prepare nitrogen **in the laboratory** is by heating a solution of sodium nitrite ($NaNO_2$) and ammonium chloride (NH_4Cl). These two compounds form the unstable compound ammonium nitrite (NH_4NO_2), which decomposes into nitrogen and water, thus:—



Small quantities of nitrogen may be readily obtained by heating ammonium dichromate ($(NH_4)_2Cr_2O_7$).

141. Physical and chemical properties of nitrogen.—Nitrogen is a colorless, odorless gas. It is a little lighter than oxygen and air. A liter weighs 1.25 gm. (A liter of oxygen weighs 1.43 gm. and one of air 1.29 gm.) It is only slightly soluble in water.

Nitrogen does not support combustion nor sustain life. Flames are extinguished by nitrogen and animals are suffocated by it.

Nitrogen is very much less active chemically than oxygen. Indeed, it responds to none of the common tests. It is sometimes called an **inert element**. At high temperatures and under special conditions, however, nitrogen is active and forms many compounds. Thus, it combines with magnesium and a few other metals at red heat, forming nitrides, *e.g.*, magnesium nitride (Mg_3N_2). An electric current causes nitrogen to combine with oxygen and with hydrogen, forming nitrogen oxides (NO , NO_2) and ammonia (NH_3). Both reactions, if hastened by a catalyst, proceed rapidly and are utilized on an industrial scale to convert nitrogen from the air into compounds needed as fertilizers and explosives. The process of converting nitrogen gas into compounds is called “fixation of nitrogen.”

142. Uses of nitrogen.—Nitrogen on account of its inertness is used to fill some kinds of electric light bulbs, and the stem of high-boiling thermometers. It is also used

in making ammonia, nitric acid, and a nitrogen fertilizer called calcium cyanamide (CaCN_2) (§ 143).

143. Nitrogen and life. — Nitrogen, as well as oxygen, is vitally connected with life, though in a different way. All animals need nitrogen for their growth. But although we live in an atmosphere containing nearly 80 per cent of this gas, we can not assimilate it directly. The nitrogen we inhale (along with the oxygen) is exhaled again unused. The nitrogen needed by our bodies must be eaten in the form of nitrogenous food, such as lean meat, fish, and wheat.

Nor have plants, with few exceptions (see next paragraph) power to assimilate free nitrogen from the atmosphere.

Most plants take up combined nitrogen from the soil in the form of nitrates or of ammonia. Hence combined nitrogen is being constantly removed from the soil. In order to restore it, a nitrogen compound must be added, *e.g.*, sodium nitrate (NaNO_3), calcium nitrate ($\text{Ca}(\text{NO}_3)_2$), ammonium chloride (NH_4Cl), ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$), or calcium cyanamide (CaCN_2). A substance



FIG. 62. — A plant with nodules on the roots.

or mixture which restores nitrogen (or some other chemical element like phosphorus or potassium) to the soil is called a **fertilizer**.

Leguminous plants, such as peas, beans, and clover, get nitrogen from the air (in the loose soil) by means of bacteria, which are in nodules on their roots (Fig. 62). The bacteria change the nitrogen into compounds which can be utilized by the growing plant. Sometimes this process is also called “fixation of nitrogen.”

144. Air is a mixture and not a compound. — Air is a mixture of several gases. Oxygen, nitrogen, and argon

are the three ingredients that are always present in nearly constant proportions. Variable proportions of water vapor and carbon dioxide are always found, and also small quantities of compounds related to ammonia and nitric acid. Near cities the air may contain considerable dust, sulfur compounds, and acids; at the ocean some salt is found.

The following facts show that air is not a compound but a mixture of gases: —

(1) The proportion of oxygen and of nitrogen is not fixed but varies between small limits. Therefore air does not have a constant composition and can not be represented by a formula.

(2) When nitrogen and oxygen are mixed in approximately the proportions that form air, the product is identical with air, but the act of mixing gives no evidence of chemical action, *e.g.*, no heat or light is produced.

(3) When air is dissolved in water, a larger proportion of oxygen than nitrogen dissolves. If the oxygen and nitrogen were combined, the dissolved air would contain the same proportions of oxygen and nitrogen as the original air.

(4) When air is liquefied and allowed to evaporate, the nitrogen escapes first (§ 156). If air were a compound, liquid air would evaporate as a whole.

145. Proportions of the main ingredients of air. — The normal proportions (by volume) are nitrogen 78.06 per cent, oxygen 21, and argon 0.937. These numbers are often rounded off to nitrogen 78, oxygen 21, and argon 0.94.

146. "Composition" of air. — Air near the surface of various parts of the globe shows such uniformity in the proportions of the main ingredients that chemists have fallen into the habit of applying the term *composition* to air.

The proportion of oxygen in the air can be readily found in the laboratory by two methods. (1) A known volume of air is shaken in a closed bottle with a mixture of pyrogalllic acid and sodium hydroxide; this solution absorbs the oxygen and leaves the nitrogen and argon unchanged. (2) A graduated glass tube, containing a known volume of air, is inverted in a jar of water, and a piece of phosphorus attached to a wire is pushed up into the tube (Fig. 63). The oxygen combines with the phosphorus. In a few hours the phosphorus is removed, and the volume of residual gas is read.

In each process the difference between the first and last volumes is oxygen. There is no simple way of separating the nitrogen and argon.

147. Water vapor in the air. — Water vapor is always present in air, owing to constant evaporation from the ocean and other bodies of water. The per cent in a given place depends on the temperature, though it is influenced also by pressure, winds, and configuration of the land. When the temperature of the air falls sufficiently, the water vapor condenses and is deposited in the form of dew, rain, fog, mist, frost, snow, sleet, or hail. The clouds are masses of minute drops of liquid water formed by condensation of the water vapor in the cold upper air. The condensation of considerable moisture forms large drops, which fall as rain.

The proportion of water vapor in the air of different regions varies between wide limits. Thus, in tropical countries it is large, while in desert countries it is small.

148. Test for water vapor in the air. — Moisture collects on the outside of a vessel containing cold water, such as a pitcher of iced water, on water pipes in a cellar.

The presence of water vapor may be shown also by exposing to the air a deliquescent substance, such as calcium chloride, which soon becomes moist (§ 94).

149. Physical comfort depends on water vapor in the air. — Our bodies have a normal and nearly constant temperature of 37°C . (98.6°F .). This temperature is maintained by the heat produced by the chemical changes in our bodies, especially the oxidation of waste tissue by the oxygen carried by the blood to all parts of the body (§ 34). This temperature is regulated partly by radiation of heat and partly by evaporation of water from the surface of the body. In moist air, evaporation proceeds too slowly; in dry air, too fast. In either case, we are uncomfortable, and try in various ways to become comfortable. Thus, we use fans and wear thin

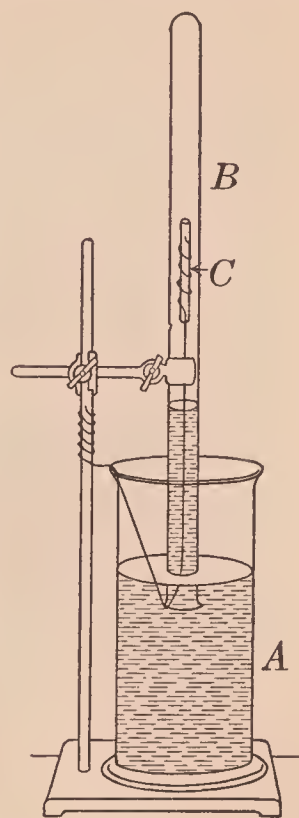


FIG. 63. — Finding the composition of air by phosphorus.

clothing to promote evaporation, or we moisten the air by exposing pans of water.

150. Carbon dioxide in the air. — Carbon dioxide is one product of the breathing of animals, the combustion of fuels, and the decay of vegetable and animal substances (§ 54). By these processes vast quantities of carbon dioxide are being constantly introduced into the air. Thus, an average person exhales about 1000 gm. of carbon dioxide daily.

The proportion of carbon dioxide in ordinary air is 3 to 4 parts in 10,000 parts of air, *i.e.*, 0.03 to 0.04 per cent. In crowded rooms it may be as high as 1 per cent or even higher in unusual cases, *e.g.*, a crowded, badly ventilated room.

The proportion of carbon dioxide in the atmosphere as a whole is practically constant, owing to the mixing by winds and air currents, and largely, also, to absorption of this gas by all green plants (§ 59).

151. Test for carbon dioxide in the air. — Carbon dioxide in the air interacts with calcium hydroxide, forming a thin, white crust of insoluble calcium carbonate on the surface of the liquid. If considerable air is drawn through calcium hydroxide solution, the liquid becomes milky, because the particles of calcium carbonate are suspended in the liquid (§ 54 and Fig. 19).

152. Argon in the air. — Argon is an essential and constant ingredient of the air, the proportion being 0.937 per cent.

Argon is a colorless, odorless gas which is a little heavier than oxygen. It dissolves in water to the extent of about 4 volumes in 100.

A conspicuous property of argon is its utter lack of chemical activity. No compounds of this element have yet been prepared or discovered. On account of its inertness, argon is used to fill one kind of electric light bulb.

153. Other gases in the atmosphere. — Helium, neon, krypton, and xenon are inert gases discovered by Ramsay. With the exception of neon, they constitute an exceedingly minute proportion of the atmosphere. Like argon they do not form compounds. Helium is used to inflate dirigible airships and neon is used to produce the red illuminated advertising signs.

154. Helium. — Helium is obtained in large quantities from natural gas which issues from the ground in certain parts of the United States, *e.g.*, Kansas, Oklahoma, and Texas. The gas contains about 2.5 per cent of helium which is extracted on a large scale by a complex process and compressed into large tanks for use in airships (Fig. 64). It is a light, non-combustible gas. Both properties make helium an excellent gas for filling balloons and dirigible airships. Helium is now used instead of hydrogen as the lifting gas in the United States airships (Fig. 65).

155. Liquid air. — Liquid air is essentially a mixture of liquid oxygen and liquid nitrogen. It sometimes looks

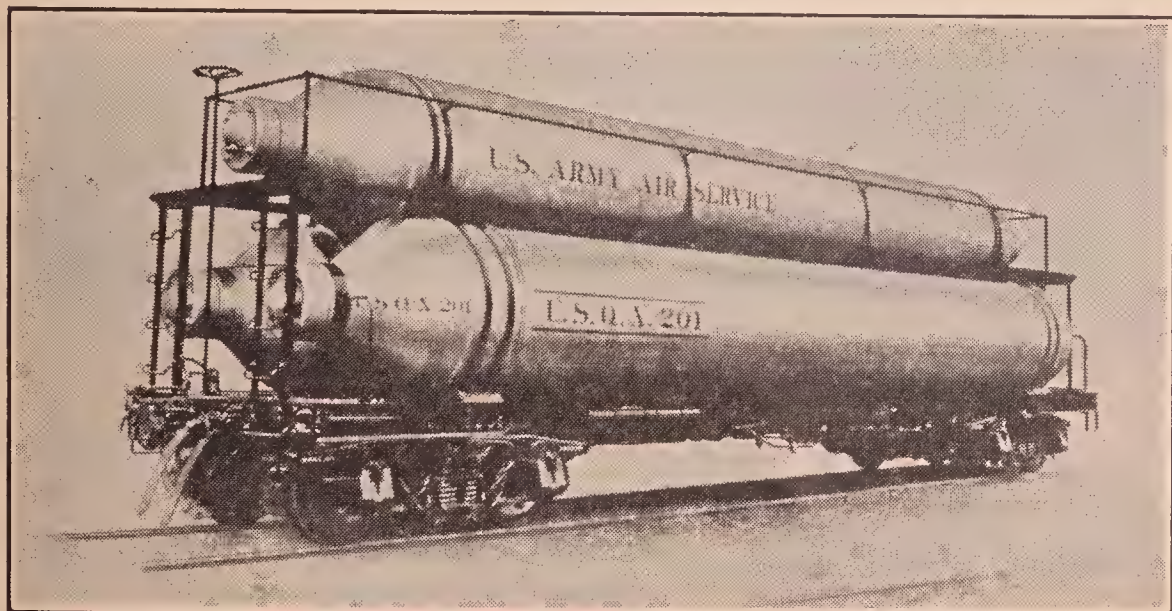


FIG. 64. — Car containing three tanks of compressed helium.

cloudy, owing to the presence of solid carbon dioxide and ice. When these solids are removed by filtering, the liquid air has a pale blue tint.

156. Properties of liquid air. — If a beaker is filled with liquid air, the latter boils vigorously, the surrounding gaseous air becomes intensely cold, frost gathers on the beaker, and in a short time the liquid air will disappear into the air of the room. If, however, liquid air is put into a Dewar flask, evaporation takes place so slowly that some liquid air will remain in the flask several days.

A Dewar flask consists of two flasks, one within the other sealed together air-tight at the top; the space between the flasks is a vacuum.

The surfaces of the flasks are coated with silver, which reflects heat and helps retard the evaporation of the liquid air. Liquid air is stored and transported in Dewar flasks. Thermos bottles are constructed like Dewar flasks.

Liquid air is a mixture and does not have a fixed boiling point, though fresh samples boil at about -190°C . If it

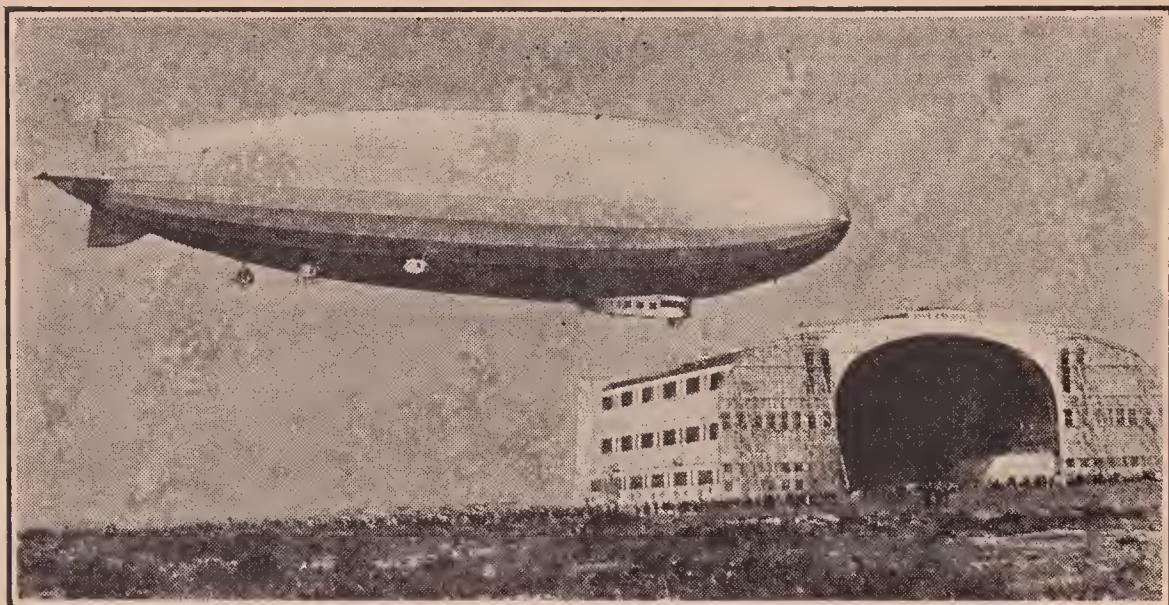


FIG. 65. — The *Los Angeles* buoyed in the air by bags of helium.

is allowed to boil in a proper apparatus, the nitrogen (boiling point -194°C .) escapes first, leaving more or less pure oxygen (boiling point -182.5°C .). The industrial separation is accomplished this way, the two gases being collected in separate tanks.

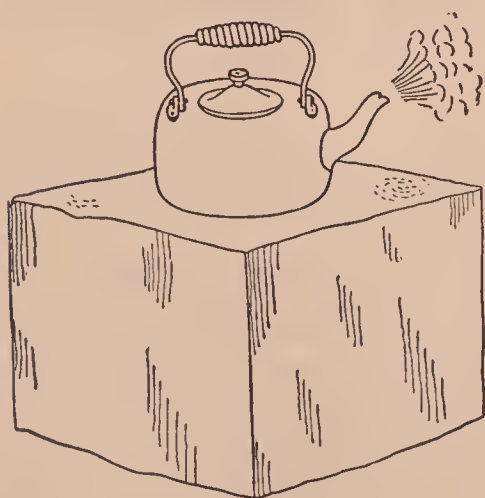


FIG. 66. — Vessel of liquid air boiling on a cake of ice.

157. Some experiments with liquid air. — A tin or iron vessel which has been cooled by liquid air is so brittle that it may often be crushed with the fingers; while a piece of rubber tubing becomes as brittle as glass. Mercury freezes so hard in liquid air that it can be used as a hammer to drive a nail.

When liquid air is poured into a vessel standing on a cake of ice (Fig. 66), the liquid air boils vigorously because the ice is so much "hotter." If a kettle of liquid air is placed over a lighted Bunsen burner, frost and ice collect on the bottom of the kettle, because the intense cold produced by the

evaporation of the liquid air in the kettle solidifies the water vapor and carbon dioxide, which are the two main products of burning illuminating gas. If water is now poured into the kettle, the liquid air boils over and the water is instantly frozen; the water is so much "hotter" than the liquid air that the latter boils more violently, and since its rapid evaporation causes absorption of heat, the water loses heat and becomes ice.

Ordinary liquid air is from one-half to one-fifth liquid oxygen, and will support combustion. A glowing stick or a red-hot rod of steel burns brilliantly in this cold liquid.

158. Manufacture of liquid air. — Liquid air is manufactured by subjecting air to a high pressure and cooling it

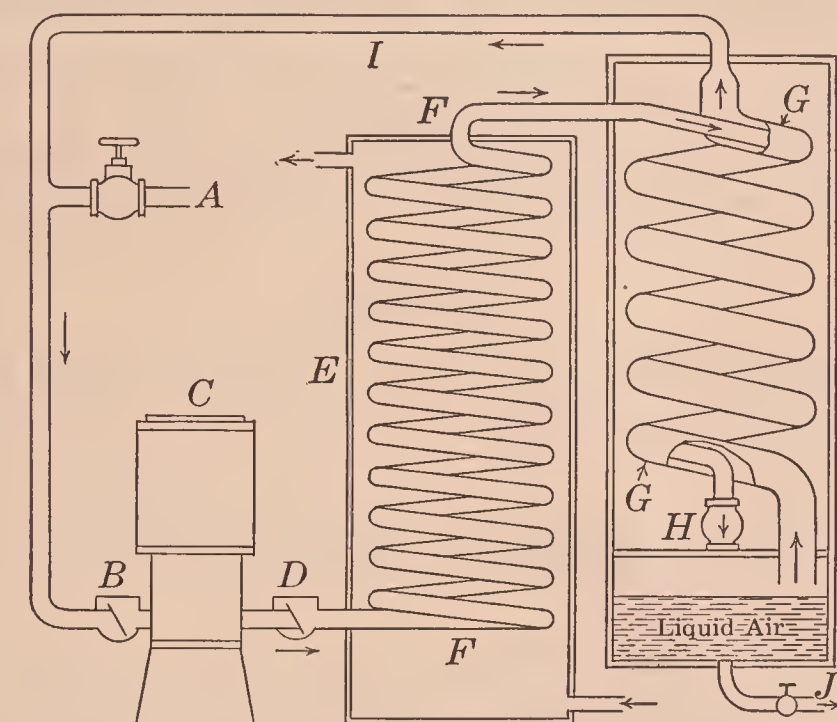


FIG. 67. — Diagram of apparatus for liquefying air.

to a low temperature. A diagram of the essential parts of a liquid air machine is shown in Fig. 67.

Air freed from moisture and carbon dioxide is forced through the valves A and B into the compressor C. Here a pump compresses the air and forces it out through the valve D into the coiled pipe FF where the heat (produced by the compression) is absorbed by running water. The compressed and cooled air is then forced along through the inner of two pipes to the valve H. This valve is small and the air escapes through it into a chamber where the pressure is lower (*e. g.*, 1 atmosphere). As the air passes through the fine opening, it expands rapidly and becomes very cold. This cold gas is made to flow back through the outer pipe G, and in so doing cools the gas flowing forward in the inner pipe.

The backward flowing gas passes through the pipe *I*, enters the machine again at *B*, is compressed, cooled, and expanded — as before. This process is continued until finally the air in the inner pipe is cooled so low that it liquefies in part, and drops from *H* into the liquid air container, from which it can be drawn off as needed through the valve at *J*.

EXERCISES

1. How is nitrogen prepared? Summarize its physical properties. Compare the chemical properties of nitrogen and oxygen.
2. What is the relation of nitrogen to the life of (a) animals and (b) plants?
3. What are the two chief ingredients of the atmosphere? The constant ingredients? The variable ingredients? The ingredients found in traces?
4. State the volumetric composition of air. How is it found?
5. Give three proofs that air is a mixture.
6. (a) How would you distinguish nitrogen from carbon dioxide?
(b) What two properties of helium make it useful in airships?

PROBLEMS

(See also Problems at the end of Chapters VIII and IX.)

1. What is the weight of air in a room $6 \times 8 \times 5$ m.? (A liter of air weighs 1.29 gm.)
2. How many kilograms of pure, dry air are needed to yield (a) 100 kg. and (b) 100 l. of oxygen (at standard conditions)?

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

- Exercise 27 — Per cent of Oxygen in Air — T.
Exercise S25 — Air and Combustion.
Exercise S26 — Water Vapor and Carbon Dioxide in Air.
Exercise S27 — Preparation and Properties of Nitrogen — T.
Exercise 4 — Heating a Known Weight of Metal in Air.

SUPPLEMENTARY SECTIONS FROM PART II

375. Atomic weights.
376. Finding approximate atomic weights.
377. Exact atomic weights.
378. International atomic weights.

CHAPTER XIII

ACIDS, SALTS, AND BASES

159. Acids. — Solutions of acids (1) have a sour taste, (2) turn blue litmus red, (3) interact with certain metals, (4) interact with oxides, hydroxides, and carbonates, and (5) conduct electricity.

Hydrogen is an essential constituent of all acids. The other constituent is a non-metal or a group of non-metals, *e.g.*, Cl, SO₄. The hydrogen in acids can be liberated by certain metals, and the compound formed by this replacement is called a salt. Many compounds have hydrogen as a constituent, but they are not acids unless they form salts by replacement of the hydrogen by a metal.

A simple **test for acids** is the change they produce in the color of litmus — blue to red. Acids cause other substances to change color, *e.g.*, phenol-phthalein from pink to colorless. Such substances are used to detect acids and are called **indicators**. Acids and other substances which redden blue litmus, or produce a specific color change in an indicator, are said to have an **acid reaction**. The presence of acids is often conveniently shown by the litmus test.

Common acids are hydrochloric acid (HCl), sulfuric (H₂SO₄), nitric (HNO₃), and acetic (HC₂H₃O₂).

160. Salts. — This class of compounds has many members and their properties vary greatly. (1) Many salts have the “salty” taste associated with common salt (sodium chloride). However, some are sour, others are bitter, and a few are tasteless. (2) Their solutions do not behave alike with litmus. Some have no effect on litmus and other indicators, and are said to be **neutral** or to have a **neutral reaction**. But

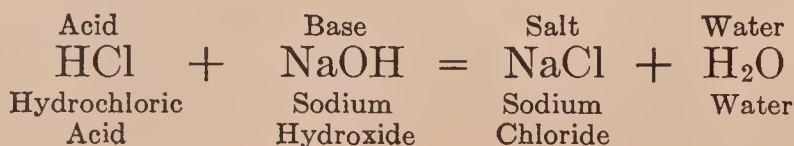
some turn blue litmus red, while others act oppositely. (3) Solutions of salts conduct electricity (§ 164).

Salts invariably have a metal and a non-metal as constituents, and most salts also have oxygen. Chlorides are examples of salts which have only a metal and the non-metal chlorine as constituents, *e.g.*, sodium chloride (NaCl), calcium chloride (CaCl_2). Examples of salts composed of a metal, a non-metal, and also oxygen are potassium chlorate (KClO_3) and sodium sulfate (Na_2SO_4); these two compounds are salts of chloric acid and sulfuric acid respectively.

161. Bases. — Hydroxides are examples of the class of compounds called **bases**. Thus, sodium hydroxide (NaOH) is a typical base. The general properties of bases differ from those of acids and salts. (1) Solutions of bases turn red litmus blue — the opposite of acids — and are said to have a **basic** or an **alkaline reaction**. Bases also turn phenolphthalein solution from colorless to rose-pink — the opposite of acids. These color changes serve as a test for bases. (2) Solutions of strong bases (*e.g.*, sodium hydroxide and potassium hydroxide) have a slippery feeling and a biting, caustic taste. Solutions of bases (3) interact with acids and form salts and water, and (4) conduct electricity.

A base is composed of a metal, combined with the group OH called hydroxyl, *e.g.*, sodium hydroxide is NaOH . This group of oxygen and hydrogen is called a radical, and is the essential part of a base, just as the hydrogen is of an acid. In fact, the oxygen and hydrogen of a base act as a unit in many chemical changes.

162. Neutralization. — When we mix a solution of an acid with a solution of a base in the proper proportions, the acid and base interact completely. The final solution has none of the characteristic properties of either an acid or a base, but it does have the properties of a salt. That is, the acid and base neutralize each other. For example, hydrochloric acid and sodium hydroxide interact, and form sodium chloride and water, thus: —



A chemical change in which an acid and a base neutralize each other and thereby form a salt and water is called **neutralization**.

Neutralization illustrates **double decomposition**, *i.e.*, a decomposition into parts and a recombination on another plan. In the chemical change just cited both the hydrochloric acid and the sodium hydroxide are decomposed and their parts are recombined into sodium chloride and water.

Neutralization may be accomplished by carefully mixing an acid and a base. But it is usually done by burettes. These are graduated glass tubes, so marked that any desired portion of the contents can be drawn off at the lower end (Fig. 68). In using burettes for neutralization, one is filled to the zero (top) mark with a solution of an acid and the other with a solution of a base — one (sometimes each) solution being of known concentration. A measured portion, say 15 cubic centimeters of the base, is drawn off into a beaker, several drops of litmus (or phenol-phthalein) solution are added, and the acid is slowly dropped in from the burette with constant stirring until one drop more shows by the change in color (after thorough stirring) that the right proportions of acid and base are present, *i.e.*, that neutralization has occurred.

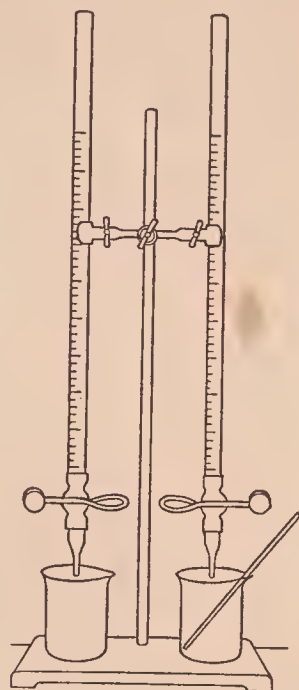
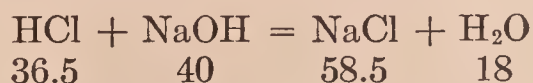


FIG. 68. — Burettes.

If we wish to find the strength of the acid, the volume of acid is read accurately. Knowing the concentration (and volume) of the base solution and the volume of the acid solution, we can calculate the exact weight of the acid needed for the neutralization of the base, and from this weight we can find the strength of the acid solution. Suppose in adding hydrochloric acid to a definite volume of sodium hydroxide solution of known strength, it was found that 1 cc. of the sodium hydroxide solution equals 1.5 cc. of the hydrochloric acid solution. The problem is to calculate the number of grams of HCl in 1 cc. of the solution of hydrochloric acid used in this experiment. Proceed as follows:

(a) First write the equation for the reaction, thus: —



This equation means that 36.5 gm. of HCl are needed to neutralize 40 gm. of NaOH.

(b) Next find the average number of cubic centimeters of hydrochloric acid solution neutralized by 1 cc. of sodium hydroxide solution.

In this illustration we assume that 1.5 cc. HCl sol. = 1 cc. NaOH sol. (Your result, of course, may be different from this value.)

(c) Next learn from the Teacher the concentration of the sodium hydroxide solution. Suppose 1 cc. of sodium hydroxide solution contains 0.00641 gm. of NaOH.

(d) Now from the equation in (a) 40 gm. of NaOH require 36.5 gm. of HCl. Then the number of grams of HCl required by 0.00641 gm. of NaOH would be found by the proportion

$$40 : 36.5 :: 0.00641 : x \qquad x = 0.00585$$

(Your result depends on the concentration of your NaOH solution.) But 0.00585 gm. of HCl would be dissolved in 1.5 cc. of hydrochloric acid (according to our supposition in (b)). Therefore, to find the number of grams of HCl that would be dissolved in 1 cc. of the acid solution, we divide 0.00585 by 1.5, *i.e.*, $0.00585 \div 1.5 = 0.0039$. *Ans.* 0.0039 gm. of HCl in 1 cc.

163. Another definition of a salt. — For the present, we may regard a salt as a compound formed from an acid and a

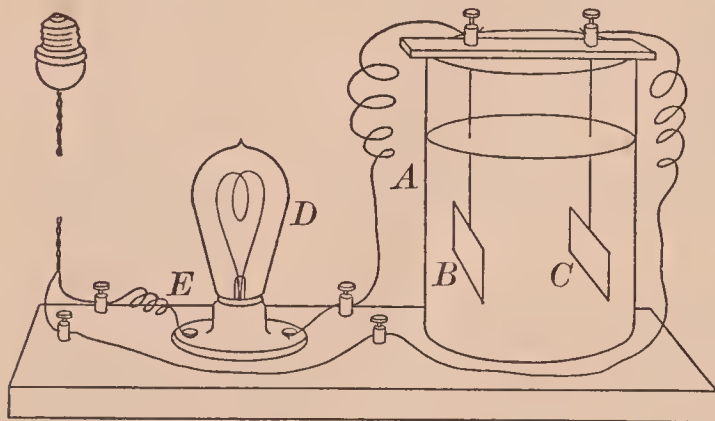


FIG. 69. — Apparatus for showing that only solutions of acids, bases, and salts conduct an electric current.

base by neutralization. That is, the metal of the base unites with the non-metal or non-metallic group of the acid, *e.g.*, Na of NaOH unites with NO_3 of HNO_3 to form NaNO_3 .

164. Solutions of acids, salts, and bases conduct electricity. —

This is a striking and fundamental property of acids, salts, and bases. It can be demonstrated by the apparatus shown in Fig. 69.

The beaker, or jar, A contains the solution into which dip two pieces of platinum, B and C, called the electrodes; through them the current enters and leaves the solution. The wire from the electrode C and the wire E from the bulb D are connected with the (direct) light current, or storage battery. The wire from the electrode B is also connected with the electric light bulb D. When the (direct) current is turned on, the bulb glows if the solution contains an acid, salt, or base. For example, if solutions of hydrochloric acid, calcium chloride, and sodium hydroxide are tried in succession, the bulb glows brightly in each case.

165. Naming acids. — The scientific names of acids are based on their composition.

The few acids containing only two elements have the prefix *hydro-* and the suffix *-ic* coupled with a simple modification of the name of the non-metallic element. Thus, bromine forms hydrobromic acid (HBr); chlorine, hydrochloric (HCl); fluorine, hydrofluoric (HF); iodine, hydriodic (HI); and sulfur, hydrosulfuric (H_2S). Remember these names.

Most acids contain oxygen, and their names are based on its proportion. The common acid of an element has the suffix *-ic*, and the acid containing one less atom of oxygen has the suffix *-ous*. Thus, nitric acid is HNO_3 and nitrous acid is HNO_2 , sulfuric acid is H_2SO_4 and sulfurous acid is H_2SO_3 . If an element forms an acid containing less oxygen than the *-ous* acid, the name of this acid has in addition the prefix *hypo-* (meaning less); *e.g.*, hypochlorous acid (HClO). If an element forms an acid containing more oxygen than the *-ic* acid, such an acid retains the suffix *-ic*, and has in addition the prefix *per-* (meaning more), *e.g.*, perchloric acid (HClO_4). A confusing point in learning the names of acids is the modification of the name of the characteristic element. These must be learned from the names of acids met in studying, *e.g.*, the element phosphorus forms phosphoric acid, and silicon forms silicic acid.

166. Naming salts. — Salts are named from their corresponding acids. In the names of salts containing only two elements or groups, the suffix *-ide* replaces *-ic* of the acid, giving the names chloride, bromide, sulfide, fluoride, and iodide. The prefix *hydro-* in the name of a binary acid is omitted from the name of the salt. Thus, the sodium salt of hydrochloric acid is sodium chloride, not hydrochloride; similarly, there are potassium bromide, lead sulfide, calcium fluoride, and sodium iodide. Two salts containing the same elements are distinguished by adding *-ous* and *-ic* to a slight modification of the name (English or Latin) of the metal — *-ous* to the one containing the smaller per cent of the non-metal. Thus, HgCl is mercurous chloride and HgCl_2 is mercuric chloride.

Most salts contain oxygen. Their names are derived

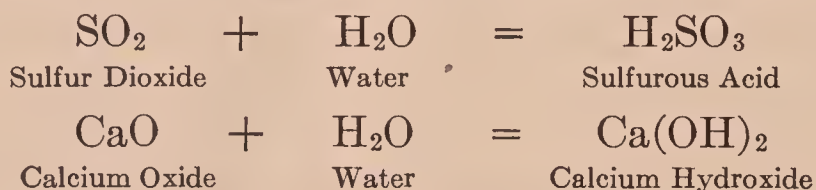
from the names of the corresponding acids by changing the suffixes *-ic* to *-ate* and *-ous* to *-ite*; the particular salt is of course distinguished by the name of the metal. The prefixes *hypo-* and *per-* are retained. The following are examples: —

ACID			CORRESPONDING SALT		
Hypochlorous acid	. .	HClO	Sodium hypochlorite	. .	NaClO
Sulfurous acid	H ₂ SO ₃	Potassium sulfite	. .	K ₂ SO ₃
Phosphoric acid	H ₃ PO ₄	Calcium phosphate	. .	Ca ₃ (PO) ₂
Permanganic acid	. .	HMnO ₄	Silver permanganate	. .	AgMnO ₄

Note that the modification of the name of some elements differs in corresponding acids and salts — sulfur- and sulf-, phosphor- and phosph-.

167. Naming bases. — Bases are named by placing the name of the metal (or group) before the word hydroxide, *e.g.*, sodium hydroxide (NaOH).

168. Formation of acids and bases from oxides and water. — We learned in § 85 that water combines directly with many oxides, *e.g.*, sulfur dioxide and calcium oxide, thus



Many oxides act similarly. The oxides of non-metals, such as carbon, sulfur, and phosphorus, produce acids. Whereas the oxides of metals, such as sodium, calcium, and magnesium, produce bases. Such oxides are called **anhydrides** — acid (or acidic) anhydrides if they form acids, and basic if they form bases.

169. Formation of salts. — Several methods have already been given. Let us review them and add others.

A. The following methods give **salts soluble in water**: —

(a) An acid and a metal — the usual method (§ 68), *e.g.*, zinc and sulfuric acid form zinc sulfate, and calcium and hydrochloric acid form calcium chloride. We can show a salt is formed by evaporating the solution to dryness and testing small portions of the residue for the parts of the salt, *i.e.*, in these two cases, for the metal part (zinc and calcium) and the non-metal part (sulfate and chloride).

(b) An acid and an oxide, *e.g.*, hydrochloric acid and calcium oxide.

(c) An acid and a carbonate, *e.g.*, hydrochloric acid and calcium carbonate.

(d) An acid and a base — neutralization, *e.g.*, hydrochloric acid and sodium hydroxide.

B. The following methods give **salts insoluble in water** : —

(a) An acid and a salt, *e.g.*, sulfuric acid and lead nitrate form insoluble lead sulfate (and nitric acid). Similarly sulfuric acid and barium chloride form insoluble barium sulfate (and hydrochloric acid).

(b) A salt and a salt, *e.g.*, sodium sulfate and lead nitrate form insoluble lead sulfate (and soluble sodium nitrate). Similarly, sodium chloride and silver nitrate form insoluble silver chloride (and soluble sodium nitrate).

(c) An acid and an oxide, *e.g.*, dilute hydrochloric acid and lead oxide (PbO) form insoluble (in cold water) lead chloride.

(d) An acid and a carbonate, *e.g.*, hydrochloric acid and lead carbonate form insoluble (in cold water) lead chloride.

One kind of salt called a **normal salt** is formed by neutralizing exactly the proper pair of acid and base. Thus, sulfuric acid and sodium hydroxide form normal sodium sulfate (Na_2SO_4) by exact neutralization. But if the acid and base are neutralized and then more sulfuric acid is added, the crystals obtained by evaporating the solution are those of acid sodium sulfate (NaHSO_4). Analogous salts are normal sodium carbonate (Na_2CO_3) and acid sodium carbonate (NaHCO_3), and normal calcium carbonate (CaCO_3) and acid calcium carbonate ($\text{CaH}_2(\text{CO}_3)_2$).

EXERCISES

1. State two characteristics of (a) acids, (b) bases, (c) salts.
2. Give the name and formula of three common (a) acids, (b) bases, and (c) salts.
3. Define and illustrate neutralization. Write an equation.
4. Write the equations for the reactions in *A* and *B* (§ 169).
5. Give the name and formula of the sodium salt of hydrochloric acid. Also of the salt corresponding to potassium, aluminum, lead, silver, manganese, zinc, and barium.

6. Apply Exercise 5 to (a) nitric acid, (b) nitrous acid, (c) hypochlorous acid.

7. Apply Exercise 5 to (a) sulfuric acid, (b) sulfurous acid, (c) permanganic acid.

8. Give the name and formula of the hydroxide of the metals enumerated in Exercise 5.

9. Give the name of these: (a) potassium salt of chloric acid, (b) calcium salt of hypophosphorous acid, (c) sodium salt of carbonic acid, (d) lead salt of chromic acid, (e) zinc salt of hydriodic acid, (f) potassium salt of perchloric acid, (g) iron salt of hydrochloric acid, (h) sodium salt of hydrofluoric acid, (i) calcium salt of persulfuric acid, (j) potassium salt of hydrobromic acid, (k) calcium salt of hydrofluoric acid, (l) sodium salt of hypophosphorous acid.

10. Complete and balance: (a) $\text{BaO} + \text{---} = \text{Ba(OH)}_2$; (b) $\text{NH}_4\text{I} + \text{---} = \text{AgI} + (\text{NH}_4)_2\text{SO}_4$; (c) $\text{Pb(NO}_3)_2 + \text{---} = \text{PbCl}_2 + \text{---}$.

PROBLEMS

1. Calculate the per cent of hydrogen in (a) hydrochloric acid, (b) sulfuric acid, (c) nitric acid.

2. Calculate the per cent of hydroxyl in (a) sodium hydroxide, (b) potassium hydroxide, (c) ammonium hydroxide.

3. What weight of HNO_3 will neutralize 27 gm. of NaOH ?

4. Calculate the formula corresponding to: (a) $\text{Ca} = 29.41$, $\text{S} = 23.52$, $\text{O} = 47.05$; (b) $\text{Na} = 39.31$, $\text{Cl} = 60.68$.

5. What weight of the salt is formed in these cases of neutralization? (a) Hydrochloric acid and 10 gm. of potassium hydroxide; (b) sulfuric acid and 37 gm. of sodium hydroxide.

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

Exercise S28 — General Properties of Acids.

Exercise S29 — General Properties of Bases.

Exercise S30 — Two Properties of Many Salts.

Exercise *28 — Behavior of Oxides with Water.

Exercise 29 — Neutralization.

Exercise 30 — Neutralization by Titration — T.

Exercise 31 — Preparation of Salts.

CHAPTER XIV

IONS AND IONIZATION

170. The ionic theory. — The properties of dilute solutions of acids, bases, and salts are best explained by the **ionic theory**. This theory was proposed in 1887 by the Swedish chemist Arrhenius (Fig. 70).

The theory is usually stated as follows: —

Acids, bases, and salts, when dissolved in water, break up into their parts, each part being charged with electricity.

This theory means that a solution of sodium chloride, for example, contains particles of electrically charged sodium and electrically charged chlorine.

171. What are ions?

— The breaking up, or dissociation as it is often called, of acids, bases, and salts in solution is

called **ionization**. The electrically charged parts are called **ions**. Each ion is a portion of a molecule. Two kinds of ions are present in every electrolytic solution, *viz.*, electro-positive ions, or **cations**, and electro-negative ions, or **anions**.

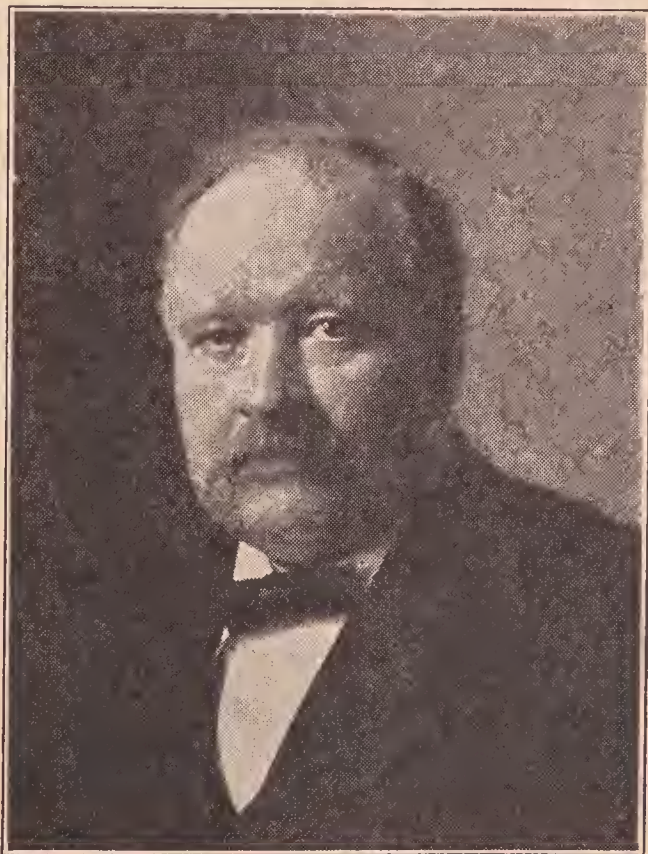


FIG. 70. — The Swedish chemist Arrhenius (1859–1927), who gave the first explanation of the properties of acids, bases, and salts.

Ions, although formed by the dissociation of molecules, are not identical with atoms. Ions are electrically charged atoms or radicals. For example, in a solution of sodium chloride the electro-positive sodium ions move about in the water without producing any hydrogen; whereas ordinary sodium interacts violently with water and produces hydrogen, as we have already seen (§ 69). Similarly, the chlorine ions circulate freely in water without escaping as chlorine gas or producing chlorine water. It should be distinctly understood that the electric charges on the ions in a solution do not come from the electricity that may subsequently be passed through the solution. The parts of the molecules become electrically charged just as soon as the molecules break up in the solution.

172. How ions are represented. — Ions are represented by chemical symbols supplemented by a plus (+) or a minus (−) sign, which shows the kind of electric charge. Thus, the ions formed by sodium chloride are Na^+ and Cl^- and from copper sulfate are Cu^{++} and SO_4^{--} . On the other hand in calcium chloride (CaCl_2) solution, each molecule dissociates into one calcium ion and two chlorine ions, *i.e.*, Ca^{++} and 2Cl^- (*not* Cl_2^-).

The solution as a whole is electrically neutral. This fact means that in the solution the sum of each kind of electric charge must be the same (*i.e.*, the total positive charge equals the total negative). It does not mean, however, that the solution must contain the same number of positive as negative ions. Thus, the ions formed by calcium hydroxide (Ca(OH)_2) are Ca^{++} and 2OH^- ; the positive charge is 2 and the total negative is 2 (*i.e.*, 2×1). In the formulas of ions, the coefficients multiply the charges. Thus, aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$) forms 2Al^{+++} and 3SO_4^{--} , making + 6 and − 6.

In ordinary chemical formulas, atoms and radicals are represented as united, *e.g.* CaCl_2 , Ca(OH)_2 . But when the molecule dissociates into independent particles (ions), we represent the ions as separate particles. That is, the Cl_2 in CaCl_2 becomes 2Cl^- or $\text{Cl}^- + \text{Cl}^-$, *not* Cl_2^- ; similarly from Ca(OH)_2 we have 2OH^- (*not* OH_2^-).

173. Acid and base defined in terms of ions. — Specific properties are exhibited by solutions of typical acids and bases. Thus, acids have a sour taste and turn litmus red; bases have a bitter taste and turn litmus blue. Solutions of acids contain hydrogen ions, and of bases contain hydroxyl ions. The properties of such solutions are doubtless largely due to the ions. According to the ionic theory, then, **an acid** is a compound whose solution contains hydrogen ions (H^+), while **a base** is a compound whose solution contains hydroxyl ions (OH^-). These definitions should be compared with those previously given (§§ 159, 161).

174. Salts and ionization. — Salts have already been defined in several ways. They are compounds (other than water) resulting from (1) the neutralization of acids and bases, (2) the substitution of a metal for the hydrogen of an acid, and (3) the substitution of a non-metal for the hydroxyl of a base (§ 163).

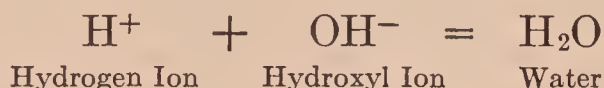
In terms of the ionic theory, salts are compounds which in solution yield neither hydrogen nor hydroxyl ions, but instead the positive ion of a base and the negative ion of an acid. Thus, sodium nitrate yields Na^+ , which is the positive ion from the base $NaOH$, and NO_3^- , which is the negative ion of nitric acid (HNO_3). An acid salt (§ 169) yields positive and negative ions, *e.g.*, $NaHSO_4$ yields Na^+ and HSO_4^- .

175. Neutralization defined in terms of ions. — In § 162 we learned that neutralization is a chemical change in which an acid and a base form a salt and water. **Neutralization**, interpreted by the ionic theory, is the combining of hydrogen and hydroxyl ions to form molecules of water. Suppose solutions of hydrochloric acid and potassium hydroxide are to be mixed in the proper proportions. The separate solutions contain respectively hydrogen and chlorine ions and potassium and hydroxyl ions. When the solutions are mixed, the hydrogen and hydroxyl ions immediately unite to form molecules of water, because water does not dissociate into ions to any appreciable extent. The final solution is thus rendered neutral by the removal of the hydrogen and the hydroxyl ions — the acidic and basic constituents respectively.

The ionic equation expressing the neutralization of potassium hydroxide by hydrochloric acid is:—



The potassium and chlorine ions move freely about in the solution. If the solution is evaporated, the ions gradually unite as the solution becomes more and more concentrated, until finally nothing remains except the neutral salt, solid potassium chloride. Since neutralization is the combining of hydrogen and hydroxyl ions to form water, the general ionic equation for neutralization is:—



176. Interpretation of certain facts by the ionic theory.—The ionic theory, like other theories, must meet one important requirement, *i.e.*, it must explain facts derived from experiment. We shall now interpret certain facts by the ionic theory.

177. Behavior of solutions toward an electric current.—Water itself conducts electricity very slightly indeed. If solutions are subjected to the action of an electric current, the results vary. Solutions of some substances conduct electricity readily; these substances are acids, bases, and salts. Whereas solutions of other substances do not conduct electricity at all.

A simple experiment enables us to find out what substances are **electrolytes** and what are **non-electrolytes**, *i.e.*, what substances form conducting solutions and what form non-conducting. We have already learned that solutions of acids, bases, and salts conduct electricity (§ 164). We can proceed in the same way with other soluble substances. The apparatus is the same as that shown in Fig. 69. The procedure is the same, except that solutions of sugar, alcohol, glycerin, etc., are put in the vessel *A*. The lamp will not glow, showing that the only solutions that conduct electricity are those from acids, bases, and salts.

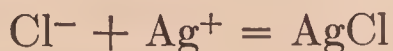
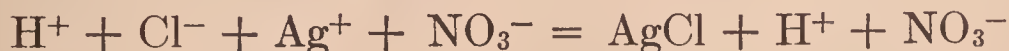
This fact is readily interpreted by the ionic theory. Solutions of acids, bases, and salts contain electrically charged particles—ions. Whereas solutions of other substances do not. Hence, when an electric current is introduced into

solutions of acids, bases, or salts, particles *already charged with electricity* are there to conduct the current. No such particles are in solutions of other substances; hence such solutions can not conduct an electric current.

178. Ionic interpretation of the chemical reactions in solutions of acids, bases, and salts. — Dry potassium chloride and dry silver nitrate do not interact chemically, but if their solutions are mixed, a precipitate of silver chloride is immediately produced. Furthermore, any dissolved chloride will interact in the same way with silver nitrate or any soluble silver salt.

Let us interpret this fact by the ionic theory. Solutions of potassium chloride and silver nitrate contain potassium ions (K^+), chlorine ions (Cl^-), silver ions (Ag^+), and nitrate ions (NO_3^-). Now when certain pairs of ions are introduced into the same solution, they react chemically. Thus, silver ions and chlorine ions combine to form insoluble silver chloride; and this precipitate serves as evidence of the chemical change. According to the ionic theory, the source of the silver ions and the chlorine ions is immaterial. And it is a fact that hydrochloric acid and solutions of different chlorides precipitate silver chloride from any solution containing silver ions, *e.g.*, silver nitrate or silver sulfate. This is the explanation offered by the ionic theory for the precipitation of silver chloride, which you will recall is the usual test for hydrochloric acid and all soluble chlorides (§ 136). The test is really a test for ions (Cl^- and Ag^+), not for substances.

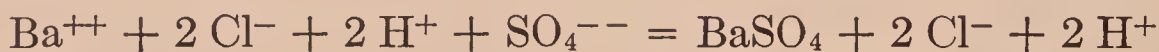
The ordinary and ionic equations for this test are —



No chemical action is observed when solutions of potassium chlorate and silver nitrate are mixed, because potassium chlorate solution contains potassium ions (K^+) and chlorate ions (ClO_3^-) — not chlorine ions (Cl^-). Hence when silver nitrate solution is added, no precipitate is formed because

silver nitrate is effective in testing for only those chlorine compounds that yield chlorine ions, not for other chlorine compounds, such as potassium chlorate (KClO_3).

Similar to the chloride test, the test for sulfuric acid and all soluble sulfates is the formation of insoluble barium sulfate (BaSO_4) upon the addition of a solution of barium chloride or any other soluble barium compound. Sulfuric acid and sulfate solutions contain sulfate ions (SO_4^{--}), which combine with barium ions (Ba^{++}) furnished by the soluble barium compound. But this test is not applicable to other sulfur compounds, such as sulfides, sulfites, and thio-sulfates, because solutions of these sulfur compounds do not contain sulfate ions. The ionic equation for a sulfate test is:—



179. Other properties besides the formation of precipitates are due to ions.— Let us consider two cases. (1) The sour taste of all acids is attributed to hydrogen ions (H^+), which are common to acids. (2) The color of certain solutions is also due to ions. Most ions are colorless, whereas solutions having a common colored ion have the same color. Thus,

copper ions (Cu^{++}) are blue, and solutions of copper salts are blue, irrespective of the color of the undissolved copper compound. Similarly, cobalt ions (Co^{++}) give pink and nickel ions (Ni^{++}) green solutions.

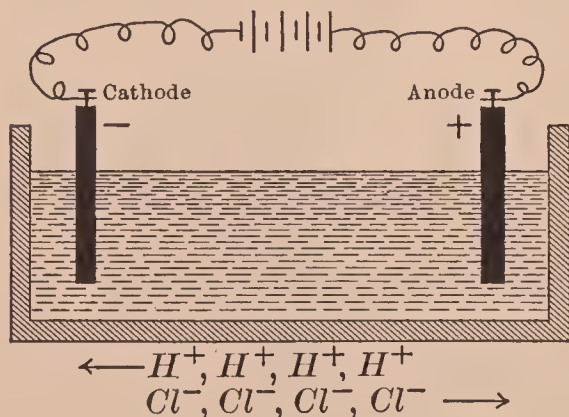


FIG. 71. — Sketch to illustrate the electrolysis of hydrochloric acid.

180. Electrolysis and ions.

— The simple experiments with solutions of acids, bases, and salts described in § 164

(in which the bulb glowed) are examples of electrolysis. **Electrolysis** is the term applied to the series of changes accompanying the passage of an electric current through a solution of an acid, base, or salt.

If an electric current is passed through a solution of hydro-

chloric acid, bubbles of gas rise from each electrode — hydrogen from the cathode or negative electrode and chlorine from the anode or positive electrode (Fig. 71).

Let us interpret this example of electrolysis by the ionic theory.

(1) The solution of hydrochloric acid contains some undissociated hydrochloric acid molecules (HCl), positively charged hydrogen ions (H^+), and negatively charged chlorine ions (Cl^-). These ions are in the solution before the electric current is passed through the solution.

(2) When the electric current is passed in, the electrodes become charged with electricity — the anode positively (+) and the cathode negatively (-).

(3) According to an old principle, bodies charged with the same kind (*e.g.*, plus) of electricity repel each other; whereas bodies charged with different kinds (*i.e.*, plus and minus) attract each other. In other words, the negative electrode (cathode) attracts the positive ions (cations) and repels the negative ions (anions). At the same time the positive electrode (anode) attracts the negative ions (anions) and repels the positive ions (cations). As a result of this attraction and repulsion the ions actually move toward the electrodes and, of course, carry their electric charges with them. In brief, anions go to the anode and cations to the cathode.

In this case, hydrogen ions (H^+) go to the cathode and chlorine ions (Cl^-) go to the anode (Fig. 71). This **migration of ions**, as it is called, was first studied carefully by the English scientist Faraday (Fig. 72), who named the charged particle "ion" from a Greek word meaning "wanderer." Thus, the term ion emphasizes the fact that when the current of electricity is passed through the solution, the two kinds of electrically charged particles (already in the solution) move toward their electrodes in two more or less orderly processions — negative ions migrating to the positive electrode and positive ions to the negative electrode.

(4) As soon as the ions come in contact with their respective electrodes they act in accordance with another long-established principle; *viz.*, they lose their electric charges. In other words, when the positive ions, or cations (H^+),

reach the cathode, the electric charges on the ions are neutralized. Electric charges, equal in quantity, though opposite in kind, are lost by the cathode, but are constantly renewed by the battery or dynamo. The hydrogen ions (H^+) once deprived of their electric charges do not regain them, but immediately become ordinary, uncharged hydrogen atoms (H) which combine and escape as molecules of hydrogen (H_2). Simultaneously, the negative ions, or anions (Cl^-), migrate to the anode, lose their charges, become chlorine atoms (Cl), unite,

and escape as chlorine molecules (Cl_2). As a final result of the electrolysis of hydrochloric acid, hydrogen and chlorine are the sole products.

181. Electrolysis often yields secondary products. — Let us consider two cases.

1. When a solution of sodium hydroxide undergoes electrolysis, hydrogen is liberated at the cathode and oxygen at the anode. The electrolysis proceeds as usual, the cations (sodium ions, Na^+) migrate to the cathode and the anions

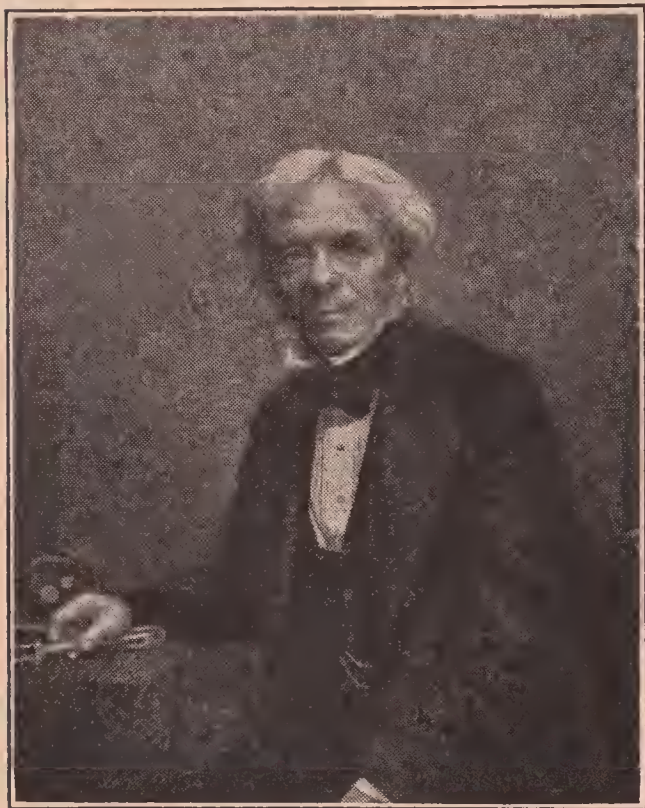


FIG. 72. — The English chemist and physicist Faraday (1791–1867), who first studied electrolysis.

(hydroxyl ions, OH^-) to the anode. But when the ions are discharged, chemical changes take place. The sodium atoms (Na), which are produced at the cathode, react with the water (in the solution), forming hydrogen and sodium hydroxide; the hydrogen escapes and the sodium hydroxide remains — dissolved in the solution. The unstable hydroxyl radicals (OH), which are produced at the anode, break down into oxygen (O_2) and water (H_2O). Hence, the final result is the production of two secondary products; *viz.*, hydrogen at the

cathode and oxygen at the anode. We might summarize the process as follows:—

(1) Ionization, $\text{NaOH} = \text{Na}^+ + \text{OH}^-$

(2) At the cathode, $2 \text{Na} + 2 \text{H}_2\text{O} = \text{H}_2 + 2 \text{NaOH}$

(3) At the anode, $4 \text{OH} = \text{O}_2 + 2 \text{H}_2\text{O}$

2. In a copper sulfate solution the ions are copper ions (Cu^{++}) and sulfate ions (SO_4^{--}). When the electric current is passed through the solution, the copper ions (Cu^{++}) migrate to the cathode, lose their electric charges, become copper atoms (Cu), and adhere as metallic copper to the cathode. The sulfate ions (SO_4^{--}) migrate to the anode, lose their electric charges, and immediately interact with the water around the anode, forming sulfuric acid (H_2SO_4), which remains in the solution (as ions), and oxygen atoms (O), which unite into molecules (O_2) and escape from the solution.

The so-called electrolysis of water (§ 97) is, strictly speaking, not the actual electrolysis of water itself but of a solution of sulfuric acid. It is interpreted as follows: Water itself does not conduct electricity, but if sulfuric acid is added, the solution is provided with hydrogen ions (H^+) and sulfate ions (SO_4^{--}), which behave as just described. After the electrolysis, the solution contains the same weight of sulfuric acid but less water — in fact, the loss of water equals the weight of the liberated gases.

182. Another definition of electrolysis. — We may now re-define or describe electrolysis as ionic migration induced by an electric current, the ions moving to their respective electrodes, where they are transformed into atoms or radicals which escape wholly or in part as elements, or which form various products by interaction with the water of the solution.

183. What ions are in a solution? — As a rule the ions formed by an electrolyte are the charged atom, or group, corresponding to the two parts of the compound. Thus, nitric acid consists of the two parts H and NO_3 , and the ions are H^+ and NO_3^- . Similarly, the parts of sodium hydroxide are Na and OH , and the ions are Na^+ and OH^- . In most cases the name of the compound is made up of the parts, *e.g.*, copper sulfate, calcium hydroxide.

The ions normally formed by the ionization of acids, bases, and salts are given in Table IV.

TABLE IV. — IONS

ELEMENT OR RADICAL	ION	ELEMENT OR RADICAL	ION	ELEMENT OR RADICAL	ION
Ammonium	NH_4^+	Barium	Ba^{++}	Aluminum	Al^{+++}
Hydrogen	H^+	Calcium	Ca^{++}	Antimony	Sb^{+++}
Mercury (ous)	Hg^+	Copper	Cu^{++}	Bismuth	Bi^{+++}
Potassium	K^+	Iron (ous)	Fe^{++}	Iron (ic)	Fe^{+++}
Silver	Ag^+	Lead	Pb^{++}	Tin (ic)	Sn^{++++}
Sodium	Na^+	Magnesium	Mg^{++}		
		Mercury (ic)	Hg^{++}		
Bromide	Br^-	Tin (ous)	Sn^{++}		
Chlorate	ClO_3^-	Zinc	Zn^{++}		
Chloride	Cl^-				
Hydroxyl	OH^-	Carbonate	CO_3^{--}		
Iodide	I^-	Chromate	CrO_4^{--}		
Nitrate	NO_3^-	Dichromate	$\text{Cr}_2\text{O}_7^{--}$		
Sulfate (acid)	HSO_4^-	Sulfate	SO_4^{--}		
		Sulfide	S^{--}		
		Sulfite	SO_3^{--}		

184. What electric charges are on ions? — As repeatedly stated, cations are positive and anions are negative. These can be selected, of course, from the table of ions. It is convenient, however, to remember these simple rules regarding the kind of charge: —

(1) Hydrogen and metals form positive ions or cations (*e.g.*, H^+ , Cu^{++}). Ammonium forms a positive ion (NH_4^+).

(2) Hydroxyl forms a negative ion (OH^-).

(3) Non-metals — except hydrogen — form negative ions or anions (*e.g.*, Cl^-).

(4) Characteristic radicals of acids and their corresponding salts form negative ions or anions (*e.g.*, NO_3^- , SO_4^{--}).

The number and kind of electric charges on an ion are the same as the valence of the corresponding atom or radical (§ 117). Thus Na^+ and Na^{+1} , Ba^{++} and Ba^{+2} , SO_4^{--} and

SO_4^{-2} , Al^{+++} and Al^{+3} . Moreover, just as the total valences of the two parts of a compound are equal, so the total number of each kind of charges (+ and -) is equal. For example, $\text{Na}^{+1} \text{Cl}^{-1}$ and Na^+, Cl^- ; $\text{Al}_2^{+3+3} (\text{SO}_4)_3^{-2-2-2}$ and 2Al^{+++} , 3SO_4^{--} . (Note: The coefficient multiplies the sign as well as the symbol, *e.g.*, $2 \text{Al}^{+++} = 2 \text{Al}$ and $+ 6$.) **Valence is defined** as the number of electric charges carried by an ion.

185. Degree of ionization of acids, bases, and salts. — Except in unusual cases solutions of acids, bases, and salts contain both molecules and ions. That is, not all the molecules dissociate into ions. The degree of dissociation depends upon the concentration of the solution and also upon the electrolyte itself. In concentrated solutions the number of molecules is large. As the solution is diluted, more and more molecules dissociate into ions.

Strong acids and bases are almost completely dissociated in dilute solutions, and weak ones are only slightly dissociated. We do not call salts “weak” or “strong,” because most of them dissociate to about the same degree.

The approximate per cent of dissociation of certain acids, bases, and salts in rather dilute solutions of the same relative concentration and at the same temperature is shown in Table V.

TABLE V. — PER CENT OF IONIZATION

SUBSTANCE	IONS	PER CENT OF IONIZATION
Hydrochloric Acid	H^+, Cl^-	92
Nitric Acid	$\text{H}^+, \text{NO}_3^-$	92
Sulfuric Acid	$2 \text{H}^+, \text{SO}_4^{--}$	61
Acetic Acid	$\text{H}^+, \text{C}_2\text{H}_3\text{O}_2^-$	1.3
Sodium Hydroxide	Na^+, OH^-	91
Ammonium Hydroxide	$\text{NH}_4^+, \text{OH}^-$	1.3
Sodium Chloride	Na^+, Cl^-	84
Silver Nitrate	$\text{Ag}^+, \text{NO}_3^-$	81
Barium Chloride	$\text{Ba}^{++}, 2 \text{Cl}^-$	76

EXERCISES

1. State the ionic theory, and several facts that support it.
2. Define and illustrate ion, anion, cation, electrode, anode, cathode, positive electrode, negative electrode.
3. What is the difference between an atom and an ion of sodium? How is each represented?
4. Name the ions in a solution of (a) hydrochloric acid, (b) sodium chlorate, (c) calcium hydroxide, (d) sodium nitrate, (e) zinc sulfate.
5. State the chemical expression for these ionized elements or radicals: (a) Hydrogen, sodium, potassium, silver, ammonium; (b) chloride, nitrate, hydroxyl; (c) calcium, barium, copper, zinc, magnesium, lead, iron (ous); (d) sulfate, carbonate; (e) aluminum, iron (ic).
6. Interpret neutralization by the ionic theory. Write the fundamental equation for neutralization.
7. Interpret by the ionic theory (a) test for a chloride; (b) test for a sulfate.
8. Define acid, base, and salt in terms of the ionic theory.
9. Define electrolysis. Interpret by the ionic theory the electrolysis of (a) hydrochloric acid, (b) sodium hydroxide, (c) copper sulfate.
10. Write ionic equations for (a) potassium chloride and silver nitrate form silver chloride and potassium nitrate, and (b) barium nitrate and sodium sulfate form barium sulfate and sodium nitrate.

PROBLEMS (Review)

(See also Problems at the end of Chapters VIII and IX.)

1. If 36 gm. of copper are heated in air until there is no farther increase in weight, what is the name, formula, and weight of the product?
Ans. 45.07 gm.
2. Equal weights of sodium and calcium interact with water, and the liberated gas is collected. Which metal yields the larger volume? Write the equation for each reaction.
3. How many grams of zinc must be used with hydrochloric acid to produce 750 cc. of hydrogen at 0° C. and 760 mm.?

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

- Exercise 32 — Electrolytes and Non-Electrolytes — T.
Exercise 33 — Electrolysis of Copper Sulfate Solution — T.
Exercise S31 — Electrolysis of Copper Sulfate Solution (Short Method) — T.

- Exercise S32 — Electrolysis of Sodium Sulfate Solution — T.
Exercise 34 — Reversible Reactions.
Exercise 35 — Colored and Colorless Ions.
Exercise S33 — Testing for Ions.
Exercise S34 — Hydrolysis of Certain Salts.
Exercise S56 — Tests for Metals.
Exercise S59 — Testing Salts for Metal and Non-Metal.

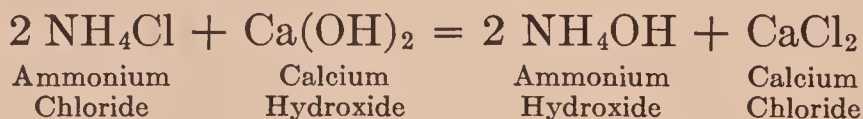
CHAPTER XV

AMMONIA — AMMONIUM HYDROXIDE — AMMONIUM COMPOUNDS

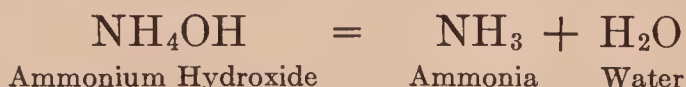
186. Introduction. — The term *ammonia* includes both the gas (NH_3) and its solution (NH_4OH). Sometimes the solution is called ammonia water, though its scientific name is ammonium hydroxide.

187. Formation of ammonia. — Ammonia is liberated during the decomposition of nitrogenous matter, *i.e.*, vegetable and animal matter containing nitrogen. If hair, leather, fur, and feathers are heated (especially with lime or soda-lime), ammonia is given off and can be detected with moist red litmus paper in the pungent gases. The formation of ammonia in this way is a **test for combined nitrogen** (§ 191, last paragraph). Soft coal contains combined nitrogen and hydrogen, and when the coal is heated, as in making illuminating gas, ammonia is liberated. This is one source of ammonium hydroxide (§ 250).

188. Preparation of ammonia in the laboratory. — Ammonia is prepared in the laboratory by heating ammonium chloride with a non-volatile hydroxide, such as moist calcium hydroxide. The equation is : —



The ammonium hydroxide is unstable, especially when heated, and decomposes into ammonia and water, thus : —



The gas is very volatile, and is usually collected by allowing it to flow upward into a bottle and displace the air.

189. Manufacture of ammonium hydroxide. — Ammonium hydroxide is manufactured by passing ammonia into water. Much of the ammonia from which commercial ammonium hydroxide is manufactured is obtained by the distillation of coal, *i.e.*, by heating the coal in closed retorts, as in the manufacture of illuminating gas and coke (§§ 250, 44). The ammonia is separated from the other gases by washing (or “scrubbing”) it out with water (§ 250 and Fig. 95). This impure solution, called ammoniacal liquor or gas liquor, is treated with lime, and the liberated ammonia is passed into tanks containing hydrochloric acid or sulfuric acid. Lime is added to this solution of ammonium chloride or sulfate, and the liberated ammonia is led into water, forming thereby the ammonium hydroxide of commerce.

Ammonium hydroxide is manufactured from the ammonia prepared by the direct combination of nitrogen and hydrogen (§§ 192, 193).

190. Physical properties of ammonia. — Ammonia is a colorless gas. It has an exceedingly pungent odor, and if inhaled suddenly or in large quantities, it brings tears to the eyes and may cause suffocation. It is light and volatile, being about one-half (0.59) as heavy as air. A liter of the gas at 0° C. and 760 mm. weighs 0.77 gm.

Ammonia gas is easily liquefied; the usual conditions are 0° C. and 4.2 atmospheres (*i.e.*, 4×760 mm.). Liquid, or liquefied, ammonia is often called anhydrous ammonia, because it contains no water. It boils at -34° C. Hence, if it is exposed to the air or warmed in any way, it changes into the gas, and in so doing absorbs considerable heat. This fact has led to the extensive use of liquid ammonia in refrigeration and in making ice (§ 194).

Ammonia gas is very soluble in water. Its solubility can be shown by the fountain experiment. (See Fig. 73 and com-

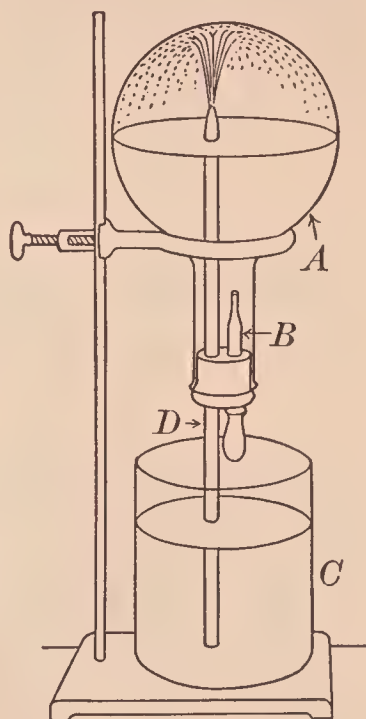


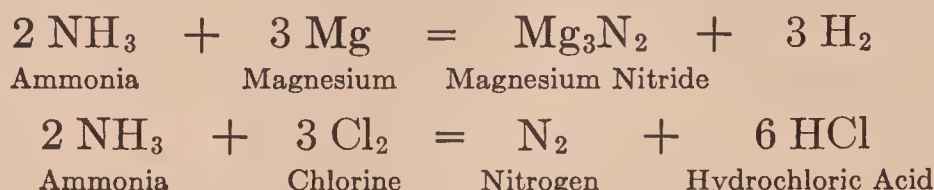
FIG. 73. — Experiment to show the marked solubility of ammonia in water.

pare § 131.) A liter of water at ordinary temperature dissolves about 700 l. of gas.

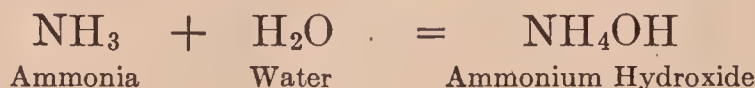
A solution of ammonia gives off the gas freely, as may be easily discovered by the odor or by the formation of dense white fumes of ammonium chloride (NH_4Cl) when the solution is exposed to hydrochloric acid (§ 132).

191. Chemical properties of ammonia. — Ammonia will not burn in air under ordinary conditions, nor will it support combustion, as the term is usually used.

Ammonia reacts with certain elements, *e.g.*, magnesium and chlorine, thus: —

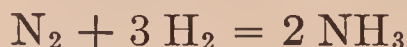


Ammonia combines directly with water, thus: —



Ammonia unites with acids and forms ammonium salts, *e.g.*, NH_3 and HCl (gas) form ammonium chloride (NH_4Cl). This reaction serves as a **test for ammonia** (§ 132).

192. Synthesis of ammonia from its elements. — Ammonia can be prepared by synthesis, *i.e.*, by direct union of nitrogen and hydrogen. The two gases unite if electric sparks are passed through their mixture. The equation is: —

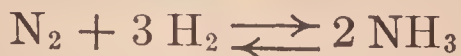


The amount of ammonia formed in a given case, however, is only a small per cent of that indicated by the equation. The small yield is due partly to the fact that ammonia itself decomposes into nitrogen and hydrogen, thus: —



If we compare these equations, we see that one is the reverse of the other. When the experiment is done in a closed tube, the two reactions proceed at the same time — one reversing the other. Such a complete reaction is called a **reversible**

reaction. The equation for a reversible reaction contains oppositely pointed arrows, thus: —



This equation is read: nitrogen and hydrogen react reversibly to form ammonia.

A reversible reaction under a given set of conditions proceeds to **equilibrium**. This means that the amounts of the substances involved in both reactions increase or decrease until the quantity of any one substance formed equals the quantity of it which is transformed in a given time. In the case of ammonia, the mixture at equilibrium is only about 2 per cent ammonia, the rest being nitrogen and hydrogen.

If ammonia is removed by introducing acid or water into the apparatus, or by some other device, its removal displaces the equilibrium (toward the NH_3) and the reaction proceeds to completion, *i.e.*, all, or practically all, the nitrogen and hydrogen combine.

193. Manufacture of ammonia from nitrogen and hydrogen by synthesis. — The reaction described in § 192 for the manufacture of ammonia proceeds slowly. To be profitable commercially, the reaction must be hastened, that is, its velocity must be increased so that more ammonia will be formed in a given time. Several factors affect the velocity of a reaction, *e.g.*, temperature, pressure, and the presence of a catalyst. In manufacturing ammonia, the best conditions are a temperature of about 400°C . and a pressure of about 200 atmospheres (*i.e.*, $200 \times 760 \text{ mm.}$). Under these conditions the yield is from 5 to 8 per cent.

Even under these conditions the velocity of the reaction is too slow for industrial use. Hence a catalyst is used to speed up the reaction. One catalyst is iron containing small amounts of potassium and aluminum oxides. Ammonia made directly from its elements is called **synthetic ammonia**.

During the World War large quantities of ammonia were manufactured in Germany by this process, called the Haber process. It is in operation in Germany and also in the United States at the present time.

A diagram of the essential parts of the apparatus for manufacturing ammonia from nitrogen and hydrogen is shown in Fig. 74. The mixture of purified nitrogen and hydrogen is passed through *A* into the compression vessel *B*, and forced through *C* into the reaction chamber *D*. Here the mixture comes in contact with the catalyst and is changed in part into ammonia. The mixture of ammonia and uncombined gases passes into the coiled pipe in the vessel *E* which contains a circulating, very cold liquid (entering at *J* and flowing out at *K*). The ammonia condenses to a liquid and accumulates in *F*, while the uncombined nitrogen and hydrogen pass along through the valve *G* and the pipe *H* into *D* again. The liquefied ammonia is drawn off through *I*.

194. Liquefied ammonia as a refrigerant. — The use of liquefied ammonia in producing low temperatures in cold

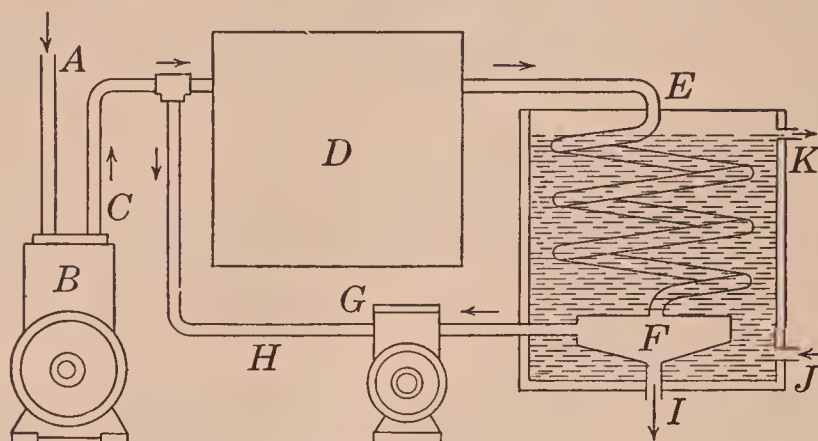


FIG. 74. — Diagram of apparatus for manufacture of ammonia from nitrogen and hydrogen.

storage plants and refrigerators (see § 221) depends upon two facts. (1) Liquefied ammonia (not ordinary ammonia solution) changes rapidly into a gas when its pressure is reduced, and (2) in so doing absorbs heat from the surrounding air or liquid. Hence, if liquefied ammonia is allowed to flow through a pipe immersed in a solution of sodium chloride or calcium chloride (technically called a brine), the ammonia evaporates in the pipe and cools the brine, which may be used directly as a refrigerant or for making ice. In some cold storage plants, packing houses, and sugar refineries, this cold brine is circulated through pipes placed in the storage rooms where a low temperature is desired (Fig. 75).

The construction and general operation of an ice-making plant is shown in Fig. 76. Liquefied ammonia is forced from a tank into a series of pipes which are submerged in a large vat *A* nearly filled with brine. Metal cans containing purified water to be frozen are immersed

in the brine, which is kept below the freezing point of water by rapid evaporation of the ammonia in the pipes. After several hours the water in the cans is frozen into cakes of ice. As fast as the ammonia gas forms

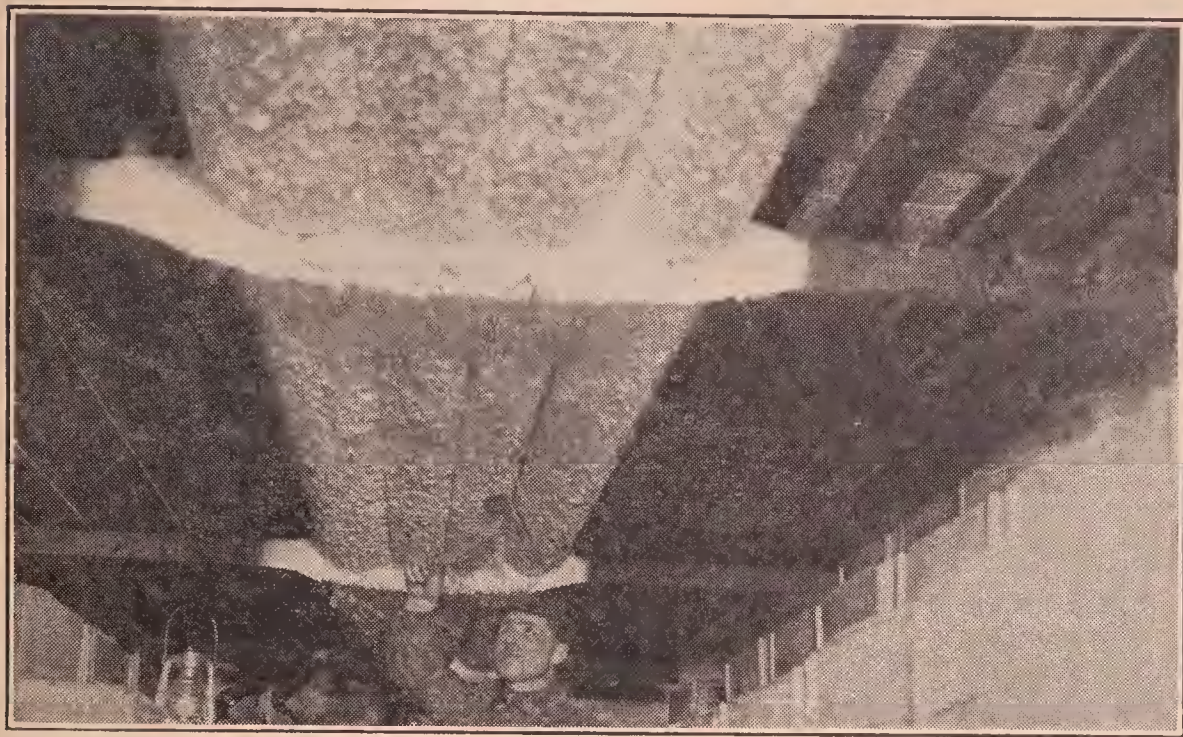


FIG. 75. — A room in a cold storage plant.

in the pipes, it is removed by exhaust pumps *E* into another set of pipes *C*, where it is condensed into liquefied ammonia and conducted through *D* into the other set of pipes ready for renewed use.

In cold storage plants the cold brine is circulated through pipes *F* to the various rooms *B*.

195. Ammonium hydroxide. — Ammonia combines with water to some extent and forms a solution of ammonium

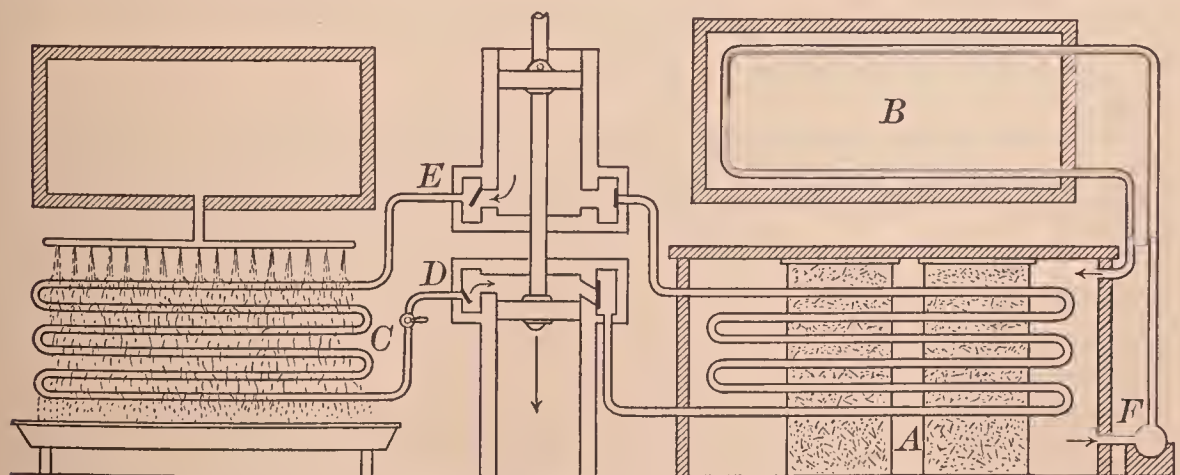
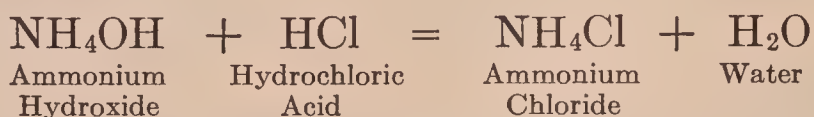


FIG. 76. — Apparatus for using liquefied ammonia to produce low temperatures.

hydroxide (NH_4OH). The NH_4 acts as a radical and in a solution becomes NH_4^+ just as K in KOH becomes K^+ .

Ammonium hydroxide is a base (§ 161), though a much weaker one than sodium hydroxide (§ 185), in spite of its pungent odor. Like other bases it turns litmus blue. Concentrated solutions have a slippery feeling. It also neutralizes acids, thus:—



Ammonium hydroxide is widely used as a cleansing agent (especially for the removal of grease), and is sold under the names “ammonia” and “household ammonia.” Large quantities are consumed in the manufacture of dyestuffs, sodium bicarbonate (§ 279), and ammonium compounds.

196. Ammonium salts.—These salts, like the base ammonium hydroxide, contain a group of atoms which acts chemically like an atom of a metal. This group is called **ammonium**, and its formula is NH_4 ; in solution it is $(\text{NH}_4)^+$. Ammonium has not been isolated from its compounds. Ammonium, like hydroxyl (§ 161, last paragraph), is a radical, because it is the root or foundation of a series of compounds and in many chemical changes passes as a unit from one ammonium compound to another.

Ammonium salts decompose when heated with sodium hydroxide or moist calcium hydroxide (§ 188); ammonia is the conspicuous product. This reaction is a **test for ammonium compounds**. Ammonium salts are highly ionized in solution and give the ion NH_4^+ .

There are many ammonium salts. **Ammonium chloride** (NH_4Cl) is formed by the neutralization of ammonium hydroxide (a base) by hydrochloric acid. It is manufactured by passing ammonia into hydrochloric acid. The crude product is often called *muriate of ammonia* to indicate its relation to *muriatic acid* (the commercial name of hydrochloric acid). It is used in some types of batteries (*e.g.*, dry cells), and as an ingredient of soldering fluids and of fertilizers.

Crude ammonium chloride is purified by heating it gently in a large iron pot with a dome-shaped cover; the ammonium chloride volatilizes and then crystallizes quickly in the pure state as a fibrous mass on the inside of the cover; the non-volatile impurities remain behind in the

vessel. This process of purification is called **sublimation**. The product is a **sublimate**. Sublimed ammonium chloride is often called sal ammoniac.

Ammonium sulfate $((\text{NH}_4)_2\text{SO}_4)$ is a grayish or yellowish solid. It is used as an ingredient of fertilizers, since it is a cheap, soluble salt containing considerable nitrogen (§ 143).

EXERCISES

1. How is ammonium hydroxide manufactured?
2. State the conspicuous properties of ammonia.
3. Define and illustrate (by ammonia) (a) reversible reaction, (b) equilibrium, (c) displacement of equilibrium, (d) catalyst.
4. State these reactions in the form of equations: (a) preparation of ammonium hydroxide from ammonium chloride and calcium hydroxide, (b) decomposition of ammonium hydroxide into ammonia and water, (c) nitrogen and hydrogen react reversibly to form ammonia.
5. Describe the manufacture of ice by liquid ammonia.
6. State the test for (a) ammonia and (b) ammonium compounds.
7. Complete and balance: (a) $\text{NH}_4\text{OH} + \text{---} = (\text{NH}_4)_2\text{SO}_4 + \text{---}$; (b) $\text{NH}_3 + \text{---} = \text{N}_2 + \text{HCl}$.

PROBLEMS

1. How many grams of ammonia (NH_3) can be obtained from 1 kg. of ammonium chloride and sufficient calcium hydroxide?
2. What weight of ammonium chloride (95 per cent pure) is needed for the preparation of 60 gm. of NH_3 ?
3. How many grams of ammonium chloride can be made from ammonium hydroxide and 100 gm. of the necessary acid?
4. What formula corresponds to the composition N = 26.17 per cent, H = 7.48, Cl = 66.35?

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

Exercise *36 — Preparation and Properties of Ammonia.

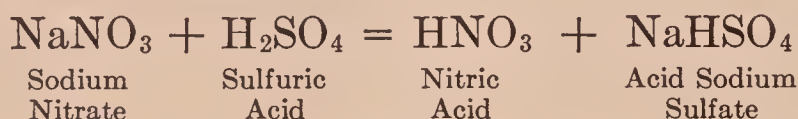
Exercise S35 — Preparation of Ammonia from Various Substances.

CHAPTER XVI

NITRIC ACID — NITRATES

197. Preparation of nitric acid. — Nitric acid is prepared in the laboratory by heating concentrated sulfuric acid with sodium nitrate (NaNO_3).

The chemical change at a moderate temperature is expressed by the equation: —



At a high temperature and with an excess of sodium nitrate, the equation is: —



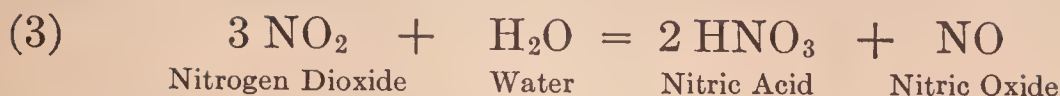
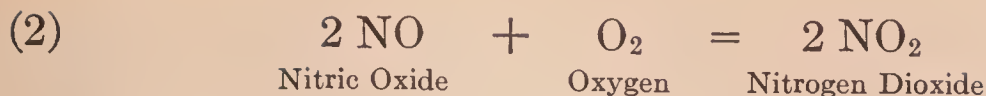
198. Manufacture of nitric acid. — Nitric acid is manufactured by several processes.

1. The first is much like that used in the laboratory. A sketch of the apparatus is shown in Fig. 77.

Sulfuric acid and sodium nitrate are heated in the cast iron retort (at the left) which is connected with quartz or stoneware tubes in which the vapor is condensed by cooling the tubes with a current of cold water (middle of sketch). The tubes are arranged so that the nitric acid first condensed runs into a reservoir for receiving concentrated acid. The vapors pass up an absorbing tower (at the right) where they are dissolved by descending water and flow out at the bottom as dilute acid.

2. A second method uses air. It depends on the fact that nitrogen and oxygen unite if subjected to the temperature of an electric arc. Three main reactions are involved: —





Two unusual conditions must be fulfilled in this process. First, the nitrogen and oxygen must be heated to a very high temperature (about 3000° C.) before they will unite to an appreciable extent. Second, the mixture of gases result-

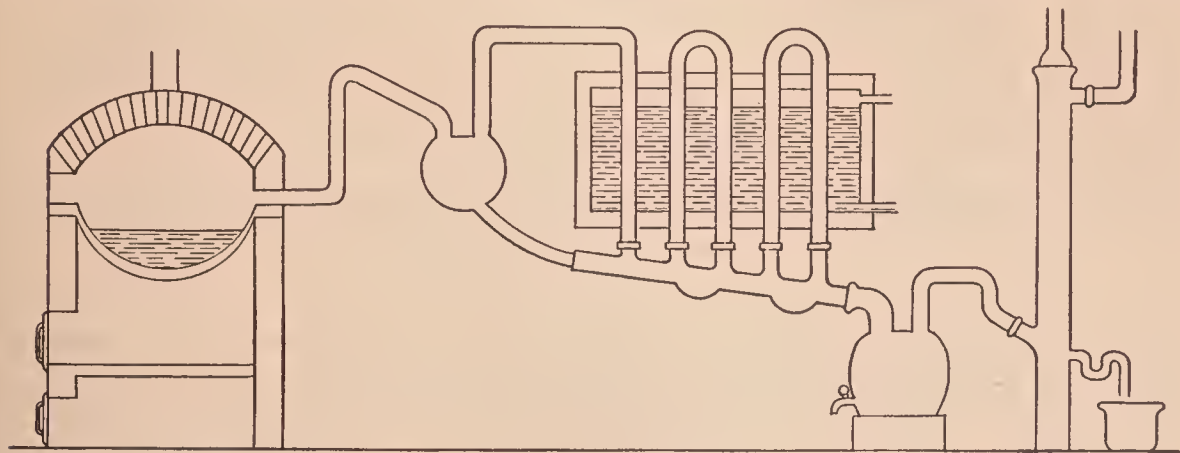
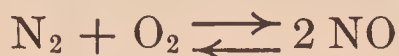


FIG. 77. — Sketch of the apparatus for manufacturing nitric acid from sodium nitrate and sulfuric acid.

ing from reaction (1) must be cooled very quickly. Reaction (1) is reversible, thus: —



The maximum quantity (only about 5 per cent) of nitric oxide is obtained at about 3000° C. At this temperature equilibrium is reached, *i.e.*, the relative proportions remain unchanged. (Compare § 192.) But just as soon as the temperature becomes lower, the reverse reaction (right to left) begins and the quantity of nitric oxide rapidly decreases. However, if the mixture is cooled very quickly, enough nitric oxide is left for reaction (2).

Reaction (2) takes place readily; the nitric oxide (NO) liberated from (1) combines with more oxygen to form nitrogen dioxide (NO₂), so that little nitric oxide (NO) is lost.

A sketch of one form of the apparatus is shown in Fig. 78 and certain parts are shown in detail in Fig. 79. Air is blown (by A) into the elec-

tric furnace *B*. Here it is raised to the proper temperature (about 3000°C.) by passing through an electric arc. In order to provide a large heating surface, the arc is spread out by powerful electromagnets

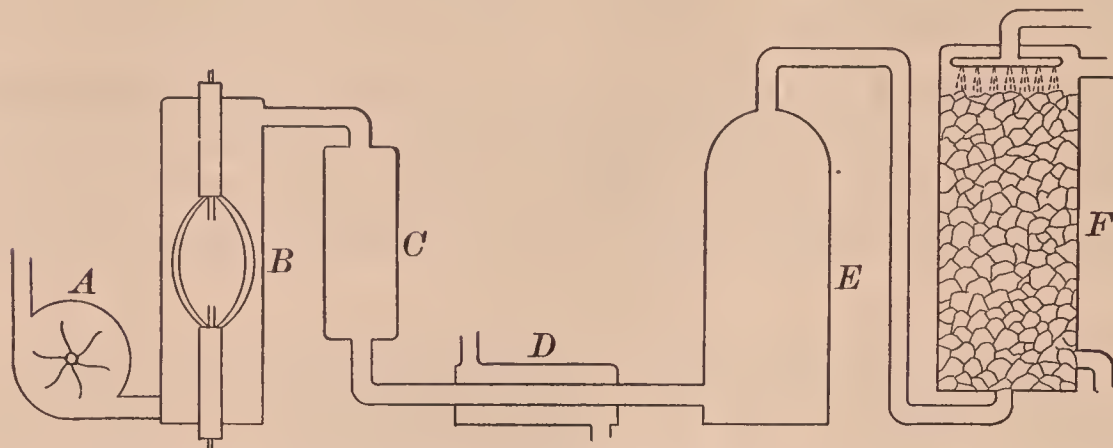


FIG. 78. — Sketch of the apparatus for the manufacture of nitric acid from nitrogen, oxygen, and water.

into a disk six feet in diameter (Fig. 79, left). The electrodes usually are hollow and are kept cool by circulating water; graphite electrodes are also used. An end view (Fig. 79, right) shows the magnets and edge of the disk. The hot gases containing the nitric oxide (NO) from the furnace are suddenly cooled in *C*, pass through the boiler *D* into the oxidizing chamber *E*, where nitrogen dioxide (NO_2) is formed.

The nitrogen dioxide passes from *E* into the tower *F*, which is filled with tiles over which water trickles. Here reaction (3) takes place and dilute nitric acid is produced. The dilute acid is concentrated or converted (by limestone or lime) into calcium nitrate. The latter is used as a fertilizer, either alone or mixed with lime.

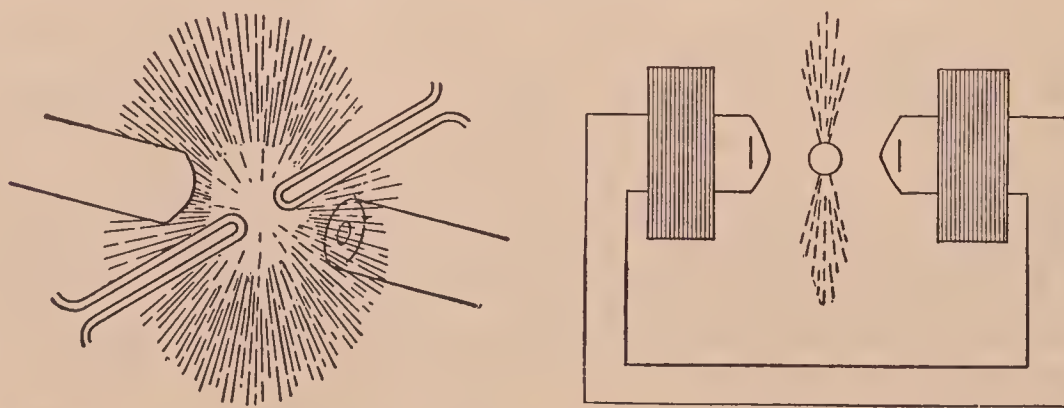


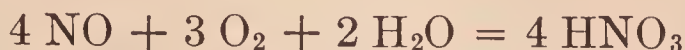
FIG. 79. — Electric arc — spread out (left) and end view (right).

3. In another process, which is rapidly coming into use, ammonia is the starting point. A heated mixture of ammonia and air is passed into fire-brick-lined chambers containing a

catalyst — usually platinum in the form of gauze. At about 1000°C ., the reaction is: —



The nitric oxide is cooled, mixed with air, and then, as in the other process, passed into towers through which water trickles, where the nitric acid is produced, thus: —



199. Physical properties of nitric acid. — Pure nitric acid is a colorless liquid, but the commercial acid is often yellow or brownish. So also, the acid that has been exposed to the sunlight is often yellow or brown, and if the light is intense, a brownish gas may often be seen in the bottle. It is somewhat volatile, and the vapor dissolves readily in water; hence the acid forms irritating fumes when exposed to air, especially moist air. (Compare § 311.)

Commercial concentrated nitric acid contains about 68 per cent of the compound HNO_3 , the rest being water.

200. Chemical properties of nitric acid. — Nitric acid is sour, turns blue litmus red, and forms salts — the nitrates. It is an unstable compound, and decomposes readily; among the decomposition products is the gas nitrogen dioxide (NO_2).

Nitric acid is a very corrosive substance and reacts readily with many substances. With nitrogenous organic substances, *i.e.*, organic substances containing nitrogen, like hair, feathers, wool, silk, finger nails, and skin it forms a yellow substance. This change is sometimes used as a **test for nitric acid** (§ 203, last paragraph). The concentrated acid causes serious burns and if spilled on the hands or face should be washed off immediately. With certain organic compounds it forms nitro-derivatives, such as nitroglycerin and nitrocellulose.

One of the decomposition products of nitric acid is oxygen. Hence nitric acid is an oxidizing agent. Hot charcoal burns brilliantly in the hot acid, while straw, sawdust, hair, and similar substances are charred and even set on fire by it.

Some organic compounds, when heated with nitric acid, are completely decomposed into carbon dioxide and water.

In the mixture of concentrated nitric and hydrochloric acids called aqua regia, nitric acid acts as an oxidizing agent (§ 135). The equation is usually written : —

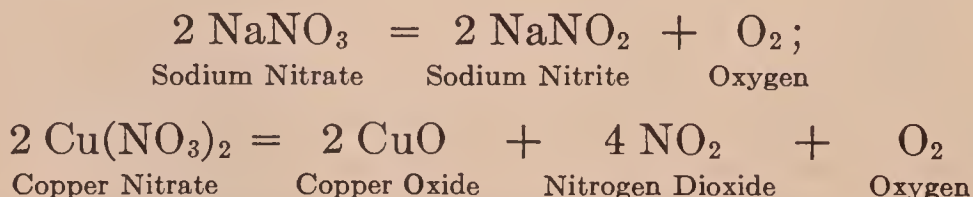


Nitric acid interacts readily and often violently with metals, metallic oxides, and hydroxides. (Compare § 132.) The products of these reactions vary, the chief ones being nitrates and nitrogen oxides (§ 203).

201. Uses of nitric acid. — Nitric acid is one of the common laboratory acids. Large quantities are used in the manufacture of nitrates, plastic substances, dyestuffs, sulfuric acid, cellulose nitrates, and explosives, *e.g.*, guncotton, picric acid, and TNT (tri-nitrotoluene).

202. Nitrates. — Nitric acid forms salts called nitrates. They are prepared by the methods usually used for salts, *i.e.*, the interaction of nitric acid and metals or metallic oxides and the neutralization of hydroxides by nitric acid.

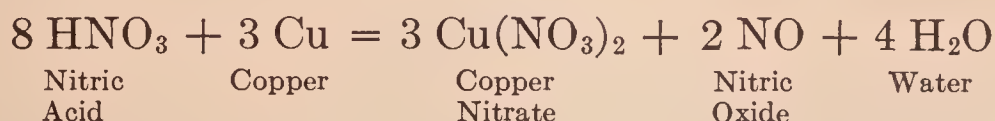
Many nitrates are white solids ; but those of copper, nickel, and cobalt are blue, green, and dark red respectively. The nitrates of most metals are soluble in water. Their solutions are frequently used in the laboratory. The solids behave in various ways when heated. Equations illustrating typical reactions are : —



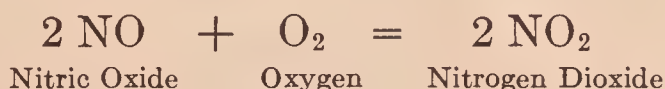
Since many nitrates, when heated, give up oxygen, they are powerful oxidizing agents. Thus, when potassium nitrate (KNO_3) is dropped on hot charcoal, the charcoal burns vigorously. This kind of chemical action is called **deflagration**. Nitrates are ingredients of gunpowder and fireworks.

203. The interaction of nitric acid and metals. — This action is exceedingly vigorous. The products of the reaction vary with the metal, the concentration of the acid, and the temperature. Hydrogen is not liberated as a rule so that it can be collected, for it is oxidized at once to water, whereas the nitric acid is reduced to nitrogen compounds — usually to nitric oxide (NO) with dilute acid and to nitrogen dioxide (NO₂) with concentrated acid.

The interaction of nitric acid and copper will serve as an example of the common reactions. When moderately dilute nitric acid (sp. gr. 1.2) is poured on copper, a reddish brown gas is given off, and the liquid turns blue, owing to dissolved copper nitrate. The equation for the reaction is: —

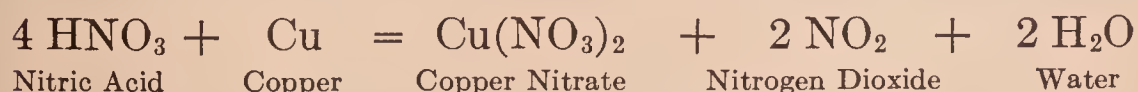


Nitric oxide is represented as a product of the interaction of nitric acid and copper. But if the reaction takes place in an open vessel, the nitric oxide, which is a colorless gas, combines with oxygen and forms the reddish brown nitrogen dioxide gas. The equation is: —

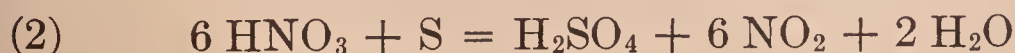
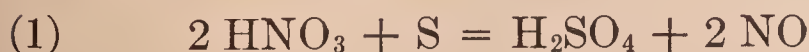


Hence we often speak of nitrogen dioxide as a product of the interaction of nitric acid and metals like copper, though it is a secondary product.

With concentrated nitric acid, copper reacts thus: —



Non-metals of course do not produce nitrates. With sulfur the reaction is represented thus ((1) is dilute and (2) is concentrated acid): —



The test for a nitrate (and of course for nitric acid) is not made, as customary, by producing a precipitate, because the nitrate ion (NO_3^-) does not form insoluble compounds with other ions. It is a color test, and is made as follows: Add to the solution of the nitrate or the nitric acid in a test tube an equal volume of ferrous sulfate solution (freshly prepared from clean ferrous sulfate and cold water). Mix well. Incline the test tube, and pour concentrated sulfuric acid cautiously down the side of the test tube. A dark colored layer appears where the two liquids meet, owing to the formation of a brown unstable compound which has the composition (approximately) $3 \text{FeSO}_4 \cdot 2 \text{NO}$.

EXERCISES

1. Summarize the properties of nitric acid.
2. What is the test for (a) nitric acid, (b) a nitrate, (c) nitric oxide?
3. Describe the interaction of nitric acid and copper and state the equations.
4. Describe fully the manufacture of nitric acid from (a) sodium nitrate, (b) nitrogen oxides, and (c) ammonia.
5. Complete and balance: (a) $\text{CuCO}_3 + \text{---} = \text{Cu}(\text{NO}_3)_2 + \text{---} + \text{---}$; (b) $\text{HNO}_3 + \text{C} = \text{NO}_2 + \text{---} + \text{CO}_2$.

PROBLEMS

(See Problems at the end of Chapters VIII and IX.)

1. Calculate the percentage composition of (a) nitric acid, (b) potassium nitrate, (c) sodium nitrate.
2. Calculate the formula and give the name of the compound corresponding to (a) $\text{O} = 76.19$, $\text{H} = 1.58$, $\text{N} = 22.22$; (b) $\text{O} = 47.52$, $\text{K} = 38.61$, $\text{N} = 13.86$.

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

- Exercise 37 — Preparation of Nitric Acid — T.
 Exercise *38 — Properties of Nitric Acid.
 Exercise *39 — Nitric Oxide and Nitrogen Dioxide.
 Exercise *40 — Test for Nitric Acid and Nitrates.
 Exercise S23 — Aqua Regia — T.

Exercise S36 — Nitrous Oxide — T.

Exercise S28 — General Properties of Acids (Nitric acid part only).

SUPPLEMENTARY SECTIONS FROM PART II

- 379. Nitrogen oxides.
- 380. Nitrous oxide.
- 381. Nitric oxide.
- 382. Nitrogen dioxide.

CHAPTER XVII

SULFUR AND SULFIDES

204. Introduction. — Sulfur is an ingredient of gunpowder. Considerable is used in the manufacture of fireworks. Large quantities are consumed in the rubber industry, especially in making automobile tires. In the paper industry, sulfur is employed in making the sulfite needed to convert the wood into pulp. Sulfur is a constituent of mixtures for killing insect pests. These mixtures, *e.g.*, lime-sulfur spray, liberate sulfur upon the injurious insect. Sulfur itself is also used as an insecticide, especially for killing *Phylloxera* — an insect which destroys grapevines.

Large quantities of sulfur are used in making sulfur compounds, *e.g.*, sulfur dioxide (SO_2) and carbon disulfide (CS_2).

205. Occurrence. — Large deposits of free sulfur occur in volcanic regions, such as Japan and Mexico. Other deposits, as in Sicily, Louisiana, and Texas, were doubtless formed by the action of microorganisms on calcium sulfate.

Sulfur compounds are abundant, *e.g.*, lead sulfide (galena, PbS), zinc sulfide (sphalerite or zinc blende, ZnS), mercuric sulfide (cinnabar, HgS), copper sulfide (chalcocite, Cu_2S , and chalcopyrite, CuFeS_2), iron sulfide (iron pyrites, FeS_2), and calcium sulfate (gypsum, $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$).

Volcanic gases often contain sulfur dioxide (SO_2), and the water of sulfur springs contains hydrogen sulfide (H_2S). Sulfur is a constituent of certain organic compounds present in onions, horseradish, mustard, and eggs. Some varieties of coal and petroleum contain sulfur compounds.

206. The United States sulfur industry. — Enough sulfur for all domestic and most foreign uses is obtained from the large deposits in southern United States, especially Texas.

The sulfur deposits are from 500 to 1000 feet deep. The sulfur is forced to the surface by an ingenious method devised by the American chemist Frasch.

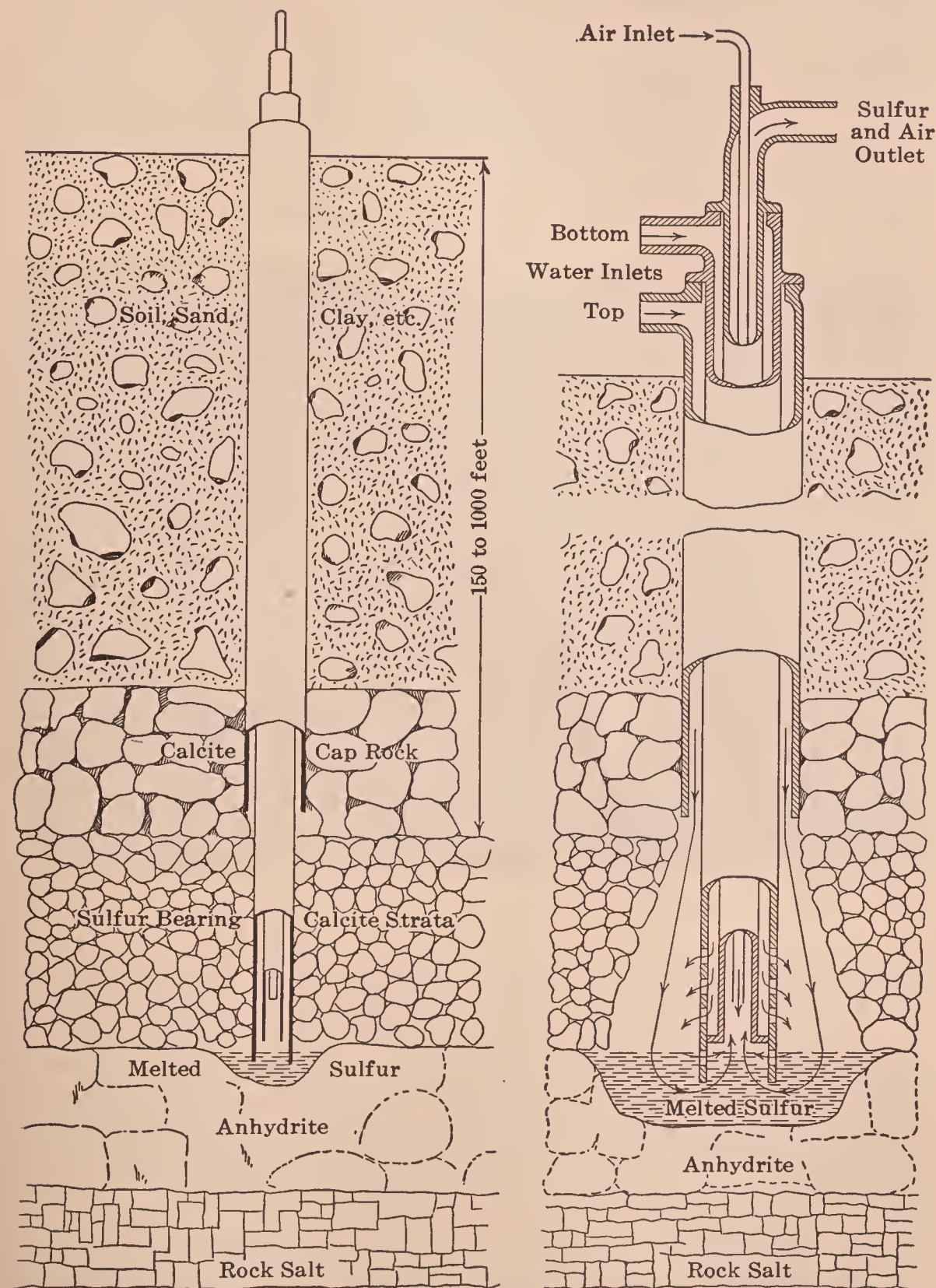


FIG. 80. — The system of pipes used in the United States to melt sulfur and bring it to the surface.

A hole is drilled through the overlying soil, sand, clay, and rock into the sulfur deposits below (Fig. 80, left). The well, as it is called, is equipped with a set of concentric pipes (Fig. 80, right). The pipes, inclosed in a casing, are driven down through the hole. The use of the pipes is clear from the diagram on the right. Through the two larger pipes water at a high temperature (170°C.) and under 100 pounds pressure is forced down to the bottom (Fig. 81). This water flows out into the porous rock and melts the sulfur (melting point about 114°C.), which collects in a pool at the bottom of the pipes. Through the smallest pipe (air inlet) hot air is forced down and forms a froth with the sulfur. This froth, owing to the pressure of the hot water and air, rises through the "sulfur pipe" (right) and flows out at the surface into large vats from

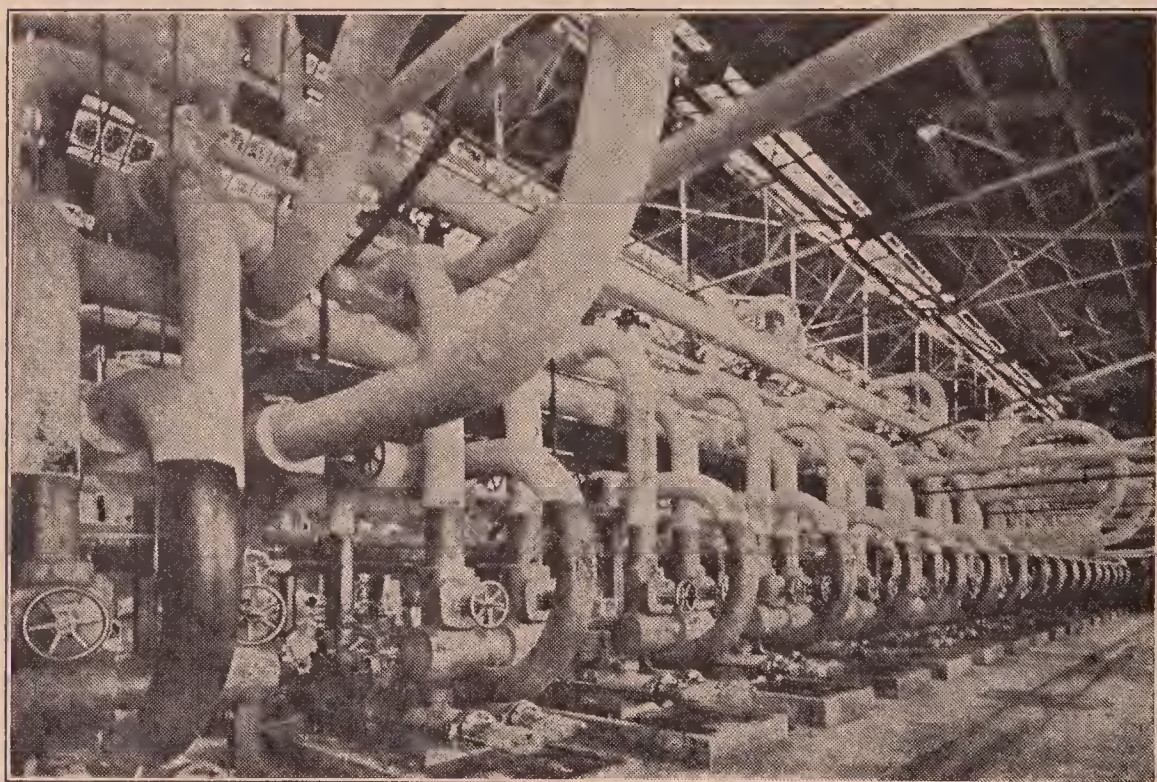


FIG. 81. — Hot water pipes and pumps.

which it is pumped into large wooden bins, where it cools and solidifies. The wooden part is then removed, leaving the sulfur as a huge block.

A single well often produces over 500 tons of sulfur a day. Some of the blocks contain as much as 100,000 tons of sulfur. When the whole block is cold, the wooden sides of the bin are removed, the sulfur is blasted into fragments, and loaded into cars by steam shovels (Fig. 82). The American sulfur industry is conducted on a prodigious scale, and yields large quantities of pure sulfur (about 99.5 per cent).

207. Physical properties of sulfur. — Sulfur is a pale yellow, brittle solid, which sometimes has a faint odor. It is insoluble in water and most acids. Most varieties of

sulfur dissolve readily in carbon disulfide (CS_2), and in sulfur chloride (*i.e.*, sulfur "monochloride," S_2Cl_2). Sulfur does not conduct electricity at all well. Its conductivity is lower than that of practically any other solid substance; this fact is sometimes expressed by saying sulfur is a good insulator. Nor does it conduct heat well, its heat conductivity being but one half that of cork and one fourth that of ice. The specific gravity of the solid is about 2, *i.e.*, it is about twice as heavy as water.

When heated slowly, sulfur melts at 114.5°C . to a thin, pale yellow liquid. As the temperature rises, the liquid

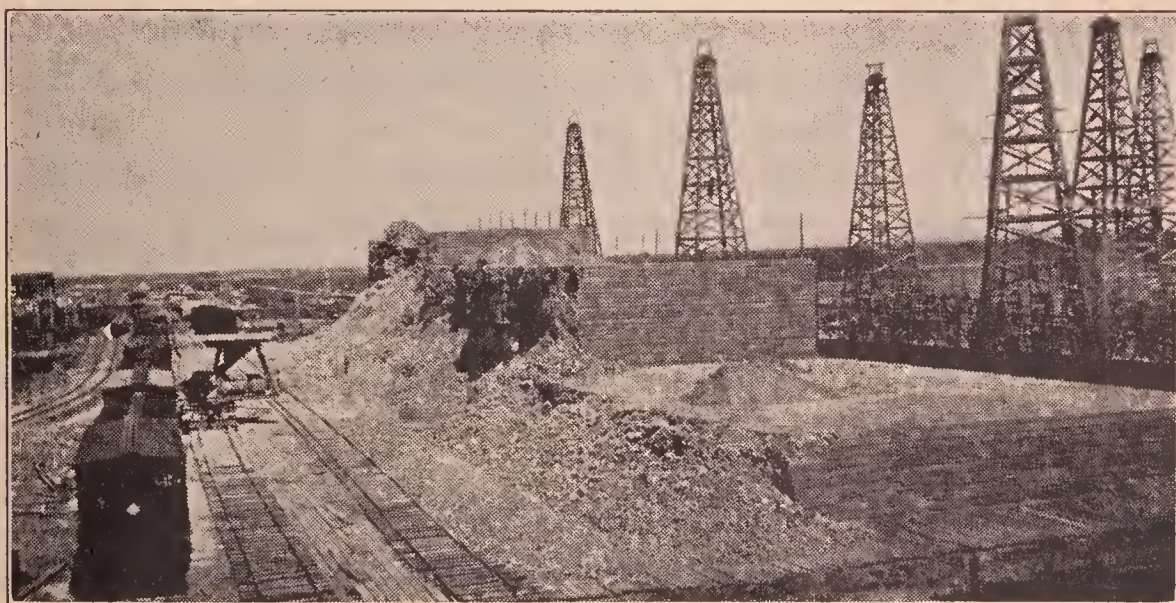


FIG. 82. — Loading sulfur into cars by a steam shovel (left), partly removed blocks of sulfur (center), derricks for drilling machinery (right).

darkens and thickens; at about 160°C . it is dark brown and viscous, at about 230°C . it is black and too thick to flow from the vessel, while at about 445°C . it becomes thin again, boils, and turns into yellow sulfur vapor.

Sulfur vapor, if formed on a large scale and then cooled, condenses to a fine powder called **flowers of sulfur**. Molten sulfur if poured in cylindrical molds forms sticks called roll sulfur or **brimstone**. Molecules of sulfur vapor at about 445°C . contain eight atoms (S_8), while at about 1800°C . the molecules contain two atoms (S_2). At about 2000°C . molecules and atoms are identical, *i.e.*, at this high temperature sulfur is monatomic (S).

208. Chemical properties of sulfur. — Sulfur is an active element. When heated, it combines readily and directly with many elements, especially oxygen. Thus, it ignites readily in the air and burns with a pale blue flame, forming sulfur dioxide (SO_2); if burned in oxygen, a little sulfur trioxide (SO_3) is also formed. Moist sulfur is oxidized to sulfuric acid slowly by exposure to air. Thus: —

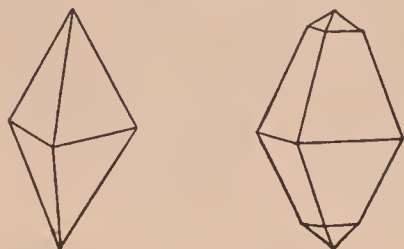


FIG. 83. — Orthorhombic crystals of sulfur.



It combines directly with most metals, forming sulfides; the reaction is often accompanied with much heat and light, as in the case of zinc, copper, and iron (§ 8). It also combines directly with carbon to form carbon disulfide (§ 49), and with chlorine to form sulfur chloride (S_2Cl_2).

209. Different modifications of solid sulfur. — There are two forms of solid sulfur.

(1) One form is called **orthorhombic**, or sometimes **rhombic**, sulfur (Fig. 83). If sulfur is dissolved in carbon disulfide and the solution evaporated slowly, sulfur is deposited as small crystals. Well-formed crystals have eight sides and belong to the orthorhombic system (Fig. 83). Crystallized native sulfur also is orthorhombic. Roll sulfur and flowers of sulfur are orthorhombic, though the crystals are often so interlaced or so small that their shape is obscured.

(2) Another variety, called **monoclinic**, is obtained by letting melted sulfur cool slowly. If sulfur is melted in a crucible and the excess of liquid is poured off as soon as crystals shoot out from the walls near the surface, the interior of the crucible will be found to be lined with long, dark yellow, shining needles (Fig. 84). They are monoclinic crystals of sulfur. In a few days they turn dull and opaque, and in time change into small orthorhombic crystals. Monoclinic sulfur is stable only if kept above 96°C .

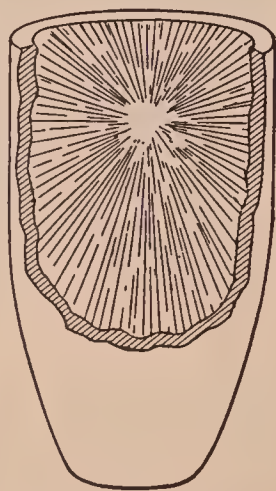


FIG. 84. — Section of a crucible showing monoclinic crystals of sulfur.

These two modifications of solid sulfur have different physical properties. Orthorhombic sulfur has the specific gravity 2.06 and melts at 112.8° C. (if heated rapidly). The corresponding values of monoclinic sulfur are 1.96 and 119.25° C.

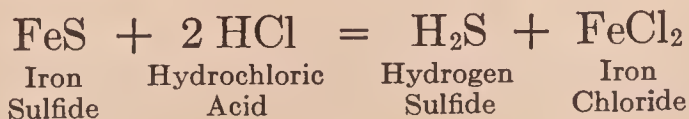
210. Different forms of liquid sulfur. — If sulfur is heated above the viscous stage or boiled and then cooled quickly by pouring it into water, a tough, rubberlike, amber-colored solid is formed. It is called amorphous or **plastic** sulfur. It is insoluble in carbon disulfide. Plastic sulfur when first formed is non-crystalline and for this reason is sometimes called amorphous ("without crystal form"). It is unstable, and soon becomes hard, brittle, and yellow; after considerable time it changes in part into orthorhombic sulfur.

211. Sulfur is an allotropic element. — The different modifications of sulfur are elementary sulfur, though they have different properties. Each burns to sulfur dioxide, and the same weight of each yields the same weight of sulfur dioxide (*e.g.*, 32 gm. of each yields 64 gm. of sulfur dioxide). Sulfur is an allotropic element (§ 52).

HYDROGEN SULFIDE AND OTHER SULFIDES

212. Occurrence of hydrogen sulfide. — This is the gaseous compound of sulfur and hydrogen with a notoriously bad smell. It occurs in the waters of some "sulfur springs" and in some volcanic gases. The air near sewers and cess-pools often contains this gas, since it is one product of the decay of organic substances which contain sulfur. The albumin in the white part of eggs contains sulfur, and when eggs decay, hydrogen sulfide is formed; hence the bad smell.

213. Preparation of hydrogen sulfide. — The gas is usually prepared in the laboratory by the interaction of dilute hydrochloric, or sulfuric, acid and ferrous sulfide. The equation is: —

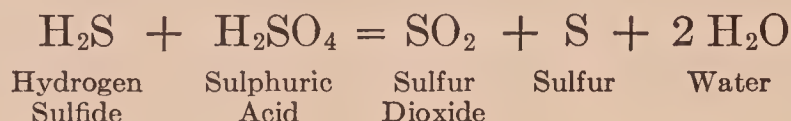


214. Properties of hydrogen sulfide. — This gas is poisonous. A little, even if diluted with air, often produces

headache and nausea, and a large quantity of the gas may prove fatal. Care should be taken to prevent its escape into the laboratory.

One volume of water dissolves about three volumes of hydrogen sulfide gas at ordinary temperatures. The solution is often called **hydrogen sulfide water**, and can be used instead of the gas in many chemical experiments; it has a weak acid reaction, and is sometimes called **hydrosulfuric acid**. In terms of the ionic theory the solution contains few ions (H^+ and S^{--}). It forms salts called sulfides (§ 215).

Hydrogen sulfide burns with a pale bluish flame, forming sulfur dioxide and water. If the supply of air is insufficient, combustion is incomplete, and sulfur and water are formed. Hydrogen sulfide reduces nitric acid and sulfuric acid; the equation for the latter reaction is:—



215. Sulfides.— These may be regarded as salts of the weak acid hydrogen sulfide, though they are not always prepared directly from hydrogen sulfide. They can be produced by the direct union of melted sulfur and metals, as in the case of iron sulfide previously mentioned (§ 8), or by exposing metals to the moist gas.

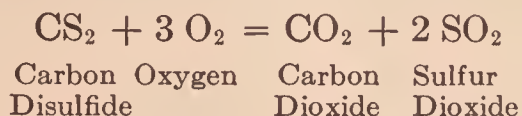
Sulfides are usually prepared in the laboratory by precipitation. That is, the gas is passed into solutions containing a metallic ion, *e.g.*, Cu^{++} ; or hydrogen sulfide water is added.

Many sulfides are black, one (zinc sulfide) is white, and several have a characteristic color. Thus, arsenic sulfide is pale yellow, manganese sulfide is flesh colored, and antimony sulfide is orange red. The color often affords a ready means of identifying a sulfide.

Copper, tin, lead, and silver react readily with hydrogen sulfide and are rapidly tarnished by exposure to the gas. Silverware turns brown or black, especially in houses heated by coal and lighted by coal gas, probably owing to the small quantity of hydrogen sulfide from these sources. A brown

film (silver sulfide) also coats silver spoons which are put into mustard, eggs, and some vegetables, such as cauliflower. Lead compounds are blackened by this gas, owing to the formation of lead sulfide. For this reason buildings painted with "white lead" paint often become dark, and, similarly, oil paintings are discolored. The blackening of paper moistened with a solution of lead nitrate or acetate is the customary test for hydrogen sulfide.

216. Carbon disulfide. — This substance, when pure, is a clear, colorless, heavy liquid, with an agreeable odor, but the commercial substance is yellow and has an exceedingly offensive smell. It is poisonous, vaporizes very readily, and is highly combustible. When the vapor burns, the equation for the reaction is: —



This liquid must be used with care. No flames should be near when carbon disulfide is being evaporated or used as a solvent. (See § 49.)

EXERCISES

1. Summarize (a) the physical properties and (b) the chemical properties of sulfur.
2. How is sulfur obtained from deposits in the United States?
3. What is (a) roll sulfur, (b) brimstone, (c) rhombic sulfur, (d) monoclinic sulfur, (e) amorphous sulfur?
4. How is hydrogen sulfide prepared? State the equation.
5. Summarize the properties of hydrogen sulfide.
6. State one or more tests for hydrogen sulfide.
7. Write these equations in the ordinary and the ionic form: (a) Lead nitrate and hydrogen sulfide form lead sulfide and nitric acid. (b) Copper sulfate and hydrogen sulfide form copper sulfide and sulfuric acid.
8. Complete and balance (a) $\text{H}_2\text{S} + \text{---} = \text{CuS} + \text{---}$; (b) $\text{CdCl}_2 + \text{---} = \text{CdS} + \text{---}$.

PROBLEMS

1. Calculate the weight of sulfur in 500 gm. of pure iron disulfide.
2. Calculate the weight of sulfur in 77 gm. of sulfuric acid containing 98 per cent of H_2SO_4 .
3. Calculate the simplest formula corresponding to (a) $\text{S} = 39$, $\text{As} = 61$; (b) $\text{S} = 29.9$, $\text{As} = 70.1$.

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

Exercise *42 — Different Forms of Sulfur.

Exercise *47 — Hydrogen Sulfide (Short Method).

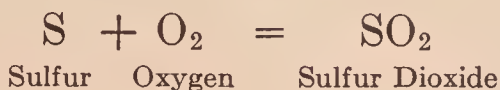
Exercise S37 — Hydrogen Sulfide — T.

Exercise S38 — Sulfides — T.

CHAPTER XVIII

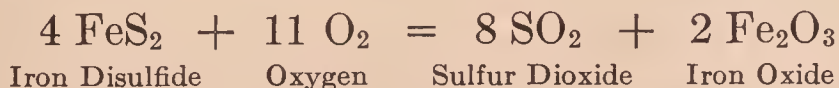
SULFUR DIOXIDE—SULFUROUS ACID—SULFURIC ACID

217. Preparation of sulfur dioxide.—Sulfur dioxide is formed by burning sulfur in air (or oxygen), thus:—



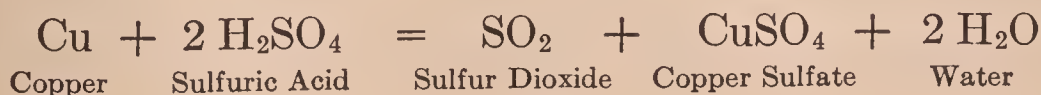
The gas is also formed when sulfur compounds are burned and sulfide ores are roasted, especially such ores as iron pyrites (iron disulfide, FeS_2) and galena (lead sulfide, PbS). It is usually one of the products of the decomposition of certain sulfur compounds, *e.g.*, sulfuric acid (H_2SO_4) and sulfurous acid (H_2SO_3).

On an **industrial scale** the gas is prepared by burning sulfur or by roasting metallic sulfides, especially iron disulfide (iron pyrites, FeS_2) thus:—

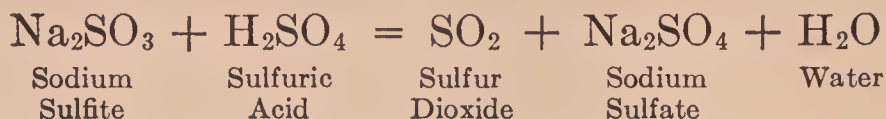


Both of these reactions (sulfur and sulfide) are utilized on a large scale in the manufacture of sulfuric acid (§§ 222–224).

In the **laboratory** two methods of preparation are used. (1) If copper and concentrated sulfuric acid are heated together, one of the products of the reaction is sulfur dioxide. The equation may be written:—



(2) More commonly dilute sulfuric (or hydrochloric) acid is added slowly to a sulfite. The equation is:—



The sulfite method is safer and more convenient, especially for a steady current of the gas.

Sometimes the gas is obtained from a cylinder of liquid sulfur dioxide (Fig. 85).

218. Physical properties of sulfur dioxide.—Sulfur dioxide is a colorless gas. Its odor is suffocating, being the well-known odor of burning sulfur. The gas is a little more than twice as heavy as air. A liter at 0° C. and 760 mm. weighs 2.9 gm.

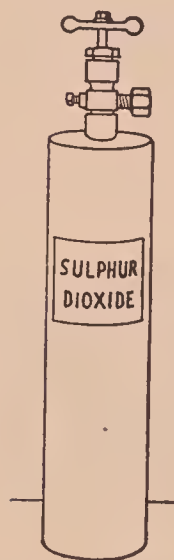


FIG. 85.—
Cylinder
of liquid
sulfur di-
oxide.

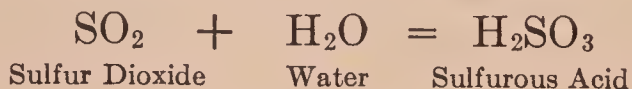
Sulfur dioxide is readily liquefied. The liquid is a common article of commerce (Fig. 85). (See § 217, end.)

The gas is very soluble in water; at 20° C. about forty volumes of gas dissolve in one volume of water. This solution is sour and reddens blue litmus; it contains sulfurous acid (H_2SO_3) besides sulfur dioxide.

Sulfur dioxide does not burn and will not support ordinary combustion.

Large quantities of sulfur dioxide are used in manufacturing sulfites and sulfuric acid (§§ 220, 222–224).

219. Sulfurous acid.—This compound is prepared by bubbling sulfur dioxide through water. Some of the gas combines with the water, thus:—



Sulfur dioxide is often called sulfurous anhydride, because it is the anhydride of sulfurous acid. Anhydrides of non-metals (*e.g.*, carbon and sulfur) are acid anhydrides, *i.e.*, non-metallic oxides which unite with water to form acids.

Sulfurous acid is unstable and decomposes readily into sulfur dioxide and water, especially when the solution is

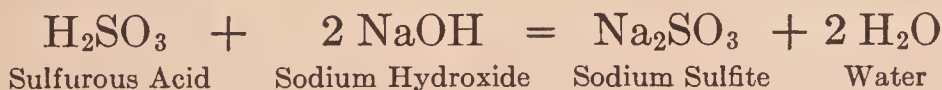
heated; solutions of sulfurous acid smell strongly of sulfur dioxide. The formation and decomposition may be represented as a reversible equation, thus:—



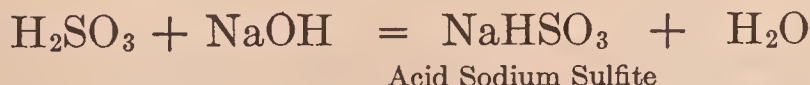
Sulfurous acid is readily oxidized. Solutions of the acid, if exposed to air, soon give a test for sulfuric acid, which is formed by the combining of the sulfurous acid with oxygen from the air. Oxidizing agents, such as potassium permanganate, produce this change quickly. Since the potassium permanganate is reduced at the same time, we can also describe this chemical change by saying sulfurous acid is a reducing agent.

220. Salts of sulfurous acid.—Sulfurous acid forms two classes of salts—the normal and the acid sulfites. When the two atoms of hydrogen in sulfurous acid are replaced by a metal, the product is a normal sulfite, *e.g.*, Na_2SO_3 , normal sodium sulfite. But if only one atom is replaced, the product is an acid sulfite, *e.g.*, NaHSO_3 , acid sodium sulfite.

Acids like sulfurous acid, which have two replaceable hydrogen atoms, are called dibasic acids, because they form salts by interaction with two different portions of a base. For example, normal sodium sulfite (Na_2SO_3) is formed when sulfurous acid is neutralized by sodium hydroxide according to this reaction:—



Whereas acid sodium sulfite (NaHSO_3), often called bisulfite of soda, is formed when half as much base is used, thus:—



Both kinds of salts yield sulfur dioxide by interaction with an acid (§ 217 (2)). The acid salt is sometimes used as the antichlor to remove the excess of chlorine from bleached cotton cloth (§ 126). It is also used in tanning, and in the manufacture of starch, sugar, and paper.

The corresponding calcium salt, acid calcium sulfite

($\text{Ca}(\text{HSO}_3)_2$), is extensively used in one process of manufacturing paper from wood. The chips of wood are "cooked" in large vessels with a solution of acid calcium sulfite, which dissolves the lignin and leaves the cellulose in the form of pulp, which is then made into paper (§ 398).

221. Uses of sulfur dioxide and sulfurous acid. — Large quantities of sulfur dioxide are used in manufacturing sulfuric acid (§ 222) and acid calcium sulfite.

Moist sulfur dioxide, which is really a solution of sulfurous acid, is used as a disinfectant and a bleaching agent. It destroys insects and organisms (or prevents their growth). It decomposes organic coloring matter, thereby forming

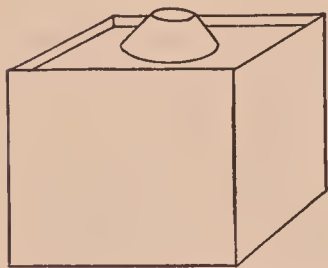


FIG. 86. — Sulfur candle for fumigation of a room.

colorless compounds. Infected clothing and rooms are sometimes fumigated with sulfur dioxide; the gas for household use may be obtained by burning a "sulfur candle" (Fig. 86). Dried fruits (*e.g.*, peaches, apricots, and apples), canned corn, cherries, and nuts are bleached by sulfur dioxide. The solution is used to bleach silk, hair, straw, paper, wool, and other substances which would be injured

by chlorine (§§ 125, 126). In some cases the bleached article, *e.g.*, a straw hat, partially regains its color or becomes yellow.

The specific effect of the moist gas can be shown by putting a wet colored flower into a bottle in which sulfur is burning; the flower soon loses its color. The general effect of sulfur dioxide on organic matter is seen in localities where considerable gas escapes, *e.g.*, near smelters and chemical works. Here trees, shrubs, and other kinds of vegetation are blighted or destroyed.

Sulfur dioxide is used as the cooling substance in one kind of "iceless" refrigerators. The liquid flows through coils, evaporates, and cools the coils, then passes through a compressor (driven by a small electric motor), becomes liquid again, and so on. By evaporation heat is absorbed and keeps the air cool in the refrigerator. (Compare § 194.)

222. Manufacture of sulfuric acid. — Enormous quantities of sulfuric acid are manufactured by two processes,

known as (1) the lead-chamber process and (2) the contact process. In each process sulfur dioxide is oxidized to sulfur trioxide, which with water forms sulfuric acid. A general equation for the essential chemical change is:—



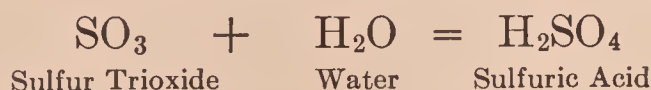
In the lead-chamber process the oxidation is accomplished by nitrogen oxides; and in the contact process it is hastened by a catalyst. The lead-chamber process is largely used when acid of a moderate concentration is needed, *e.g.*, for manufacturing phosphate fertilizer (§§ 301, 302). The contact process is used to produce concentrated acid.

223. Manufacture of sulfuric acid by the lead-chamber process.—Sulfur dioxide, air, steam, and nitrogen oxides are introduced into large lead chambers. These gases react and produce sulfuric acid, which collects on the floors of the lead chambers. This acid contains 60 to 70 per cent of the compound H_2SO_4 . For some uses, the acid needs no further treatment and can be used at once. The acid can be concentrated by heating it first in lead-lined pans and finally in quartz vessels until it contains about 94 per cent of H_2SO_4 (and has a specific gravity of 1.84).

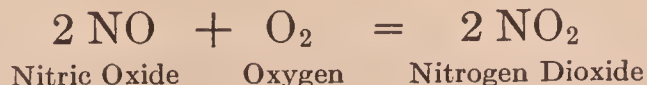
There are three main chemical changes in the lead-chamber process: (1) Sulfur dioxide is oxidized to sulfur trioxide by nitrogen dioxide, thus:—



(2) Sulfur trioxide and water form sulfuric acid, thus:—



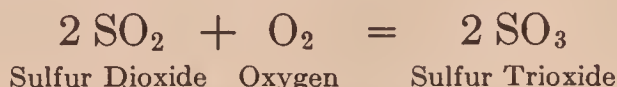
(3) Nitric oxide from (1) unites with oxygen (from the admitted air) and forms nitrogen dioxide (which is used over again), thus:—



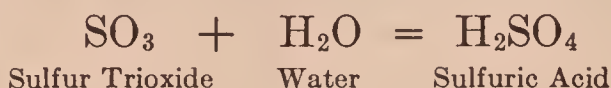
Hence, nitric oxide acts as a carrier of oxygen, so to speak,

from the (admitted) air to the sulfur dioxide. Some authorities call the nitric oxide a catalyst (§§ 22, 78, 193, 224).

224. Manufacture of sulfuric acid by the contact process. — In this process sulfur dioxide and air, well purified and heated to about 400° C., are brought in contact with a catalyst, usually platinum. The sulfur dioxide is quickly oxidized to sulfur trioxide, thus: —



The sulfur trioxide is conducted into sulfuric acid containing a little water (because it is not absorbed quickly enough by water alone) and thereby produces sulfuric acid, thus: —



The essential factor in the contact process is the catalyst. It must present a large surface for contact with the gases, be

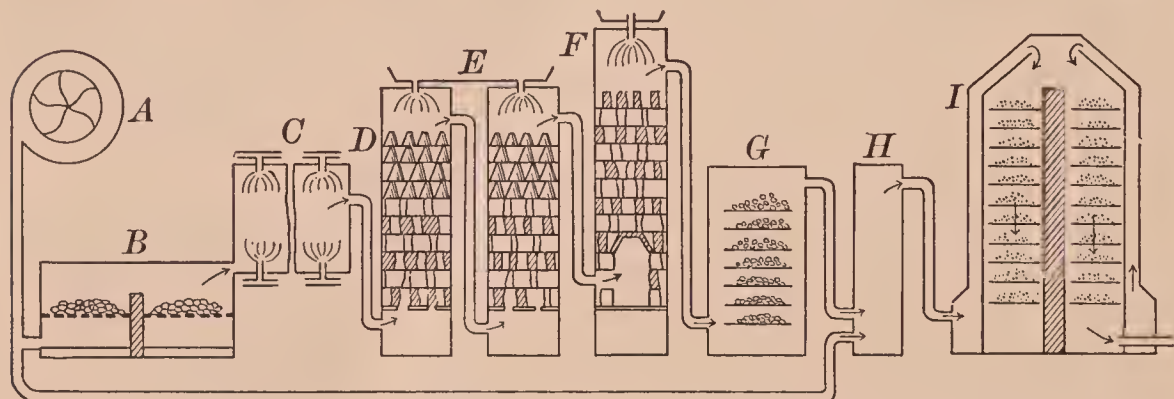


FIG. 87. — Sketch of the apparatus for making sulfuric acid by the contact process.

not easily “poisoned” by impurities in the gas, and hasten the reaction to a velocity which permits profitable operation. The best catalyst is platinum, which is coated in a very finely divided state on the surface of asbestos fibers, small lumps of magnesium sulfate, or silica gel (*i.e.*, silicic acid containing 5 to 7 per cent of water). Other catalysts may be used instead of platinum, *e.g.*, iron oxide or vanadium silicate.

The construction and operation of a contact acid plant is clear from the sketch shown in Fig. 87. The blower A forces air into the burner B, where the sulfur dioxide is formed by burning iron pyrites

(FeS_2) or sulfur. The gases pass into the dust chamber *C*, where they are freed from sulfur dust and other solid impurities; this is an important step, for dust reduces the transforming power of the catalyst. The gases, cooled by the pipe *D*, are further cleaned in the scrubbers, which contain coke wet with water (*E*) and with sulfuric acid (*F*). The next step is the removal of dust and traces of arsenic compounds (*e.g.*, arsenious oxide As_2O_3) in the purifier *G*, which would “poison” the platinum used as a catalytic agent and stop the formation of sulfur trioxide.

The purified gases (mainly sulfur dioxide) then enter the mixer and heater *H*. Here a large excess of air is introduced from the blower and the whole mixture is heated to 400°C . This temperature is carefully regulated because at 400°C . the yield of sulfur trioxide is maximum (98–99 per cent).

The purified and heated mixture of sulfur dioxide and air passes into the contact chamber *I*. Here the gases come in contact with the catalyst and form sulfur trioxide. The catalyst, if platinum, usually consists of asbestos fibers coated with a very thin layer of metallic platinum and is spread out on plates or mixed with porous material in order to provide a large contact surface.

The final step is the transformation of the sulfur trioxide into sulfuric acid by combining with water; the trioxide is passed into the absorber (not shown). This is a large earthenware jug partly filled with sulfuric acid containing 1 to 3 per cent of water. In this liquid all the sulfur trioxide combines with water; the water is replenished to maintain the required concentration in the absorber. The gases from the contact chamber *I* cannot be passed directly into pure water owing to the formation of a mist or fog which prevents absorption of the sulfur trioxide.

If fuming sulfuric acid ($\text{H}_2\text{S}_2\text{O}_7$), or oleum as it is sometimes called, is required, the sulfur trioxide is passed directly into 100 per cent sulfuric acid.

225. Physical properties of sulfuric acid.—

Sulfuric acid is an oily liquid, colorless when pure, though sometimes brown from the presence of charred organic matter, such as dust. The specific gravity of the commercial acid is about 1.84; thus it is nearly twice as heavy as water (Fig. 88). When heated, it begins to decompose and form white, suffocating fumes of sulfur trioxide at $150^\circ\text{--}180^\circ\text{C}$., and finally boils at about 338°C .

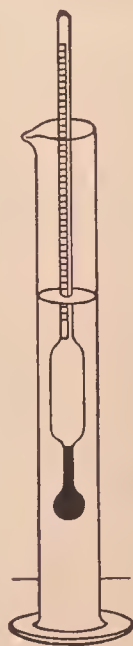


FIG. 88. — Finding the specific gravity of sulfuric acid with a hydrometer.

226. Chemical properties of sulfuric acid. — Sulfuric acid mixes with water in all proportions, and during the mixing much heat is evolved. The acid should always be poured into the water and the mixture should be stirred, otherwise the intense heat may crack the vessel or spatter the hot acid.

This tendency to absorb water is shown in many ways. The concentrated acid absorbs moisture from the air and from gases passed through it. It is often used in the laboratory to dry gases. Organic substances, such as wood, paper (cellulose $(C_6H_{10}O_5)_y$), sugar ($C_6H_{12}O_6$ and $C_{12}H_{22}O_{11}$), starch $((C_6H_{10}O_5)_x)$, and cotton, are charred by concentrated sulfuric acid (Fig. 89). Such compounds contain hydrogen

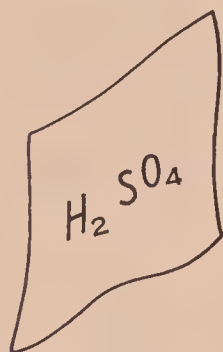


FIG. 89.—Paper charred by concentrated sulfuric acid.

and oxygen in the proportion of 2 H to 1 O, *i.e.*, in the proportion to form water; hence these two elements are abstracted and carbon alone remains. Sulfuric acid also disintegrates the flesh, often causing serious burns. If accidentally spilled on the hands or spattered on the face, it should be washed off immediately.

The interaction of sulfuric acid and metals varies. With many metals dilute sulfuric acid forms hydrogen and the corresponding metallic sulfate (§ 68). Thus, hydrogen is usually prepared in the laboratory from zinc and sulfuric acid. Some metals, however, reduce the acid to sulfur dioxide (or hydrogen sulfide). Thus, the equation expressing the reaction with copper and concentrated acid is: —



Iron is the only common metal that is not readily attacked by the concentrated acid, and advantage is taken of this property in transporting the acid in bulk in iron tank cars.

Sulfuric acid unites with ammonia (NH_3) to form ammonium sulfate $((NH_4)_2SO_4)$.

Hot concentrated sulfuric acid and carbon form sulfur dioxide and carbon dioxide. Thus:—



Dilute solutions of sulfuric acid contain an abundance of hydrogen ions (H^+) and sulfate ions (SO_4^{--}). The HSO_4^- ion is in solutions of certain concentration.

227. Uses of sulfuric acid. — Sulfuric acid is one of the most important substances. Directly or indirectly it is used in hundreds of industries upon which the comfort, prosperity, and progress of mankind depend. It is used in the manufacture of many acids (§§ 130, 198). The petroleum industry requires large amounts for refining the oil — about 20 per cent of the output. Enormous quantities are consumed in making fertilizers, alum and other sulfates, nitro-glycerin, glucose, dyes, and in various parts of such fundamental industries as dyeing, bleaching, metal cleaning (*e.g.*, pickling iron castings), refining, and metallurgy.

228. Sulfates. — Sulfuric acid is dibasic and forms two classes of salts — the normal sulfates, such as sodium sulfate (Na_2SO_4), and the acid sulfates (or bisulfates), such as acid sodium sulfate (NaHSO_4). (Compare § 220.)

Most sulfates are soluble in water; only the sulfates of barium, strontium, and lead are insoluble, while calcium sulfate is slightly soluble. Important sulfates are calcium sulfate (gypsum, $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$), barium sulfate (barite, barytes, heavy spar, BaSO_4), zinc sulfate (ZnSO_4 , and white vitriol, $\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$), copper sulfate (CuSO_4 , and blue vitriol or blue stone, $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$), iron sulfate (ferrous sulfate, FeSO_4 , and green vitriol, copperas, $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$), sodium sulfate (Na_2SO_4) and Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$), and magnesium sulfate (MgSO_4 , and Epsom salts, $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$).

229. The test for sulfuric acid or for a soluble sulfate. — The usual test is the formation of white, insoluble barium sulfate upon the addition of barium chloride (§ 178).

An insoluble sulfate, *e.g.*, calcium sulfate or barium sulfate, if fused on charcoal is reduced to a sulfide, which blackens a moist silver coin, owing to the formation of silver sulfide (Ag_2S); this is the usual test for an insoluble sulfate.

230. Sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$). — This is a salt of an unstable acid. It is sometimes incorrectly called sodium hyposulfite, or simply “hypo.” It is a white, crystalline solid, very soluble in water. The solution, used in excess, dissolves certain compounds of silver, *i.e.*, AgCl , AgBr , AgI ; hence its extensive use in photography (§ 491).

EXERCISES

1. How is sulfur dioxide prepared? Give four equations for its preparation.
2. State the properties of sulfur dioxide.
3. Define, and give the formula of, (a) a normal sulfite and (b) an acid sulfite.
4. Apply Exercise 3 to sulfates.
5. Describe the contact process of manufacturing sulfuric acid.
6. Enumerate the important uses of sulfuric acid.
7. What is (a) gypsum, (b) white vitriol, (c) green vitriol, (d) blue vitriol, (e) Glauber's salt, (f) oil of vitriol, (g) “hypo,” (h) calcium bisulfite?
8. State the test for (a) sulfuric acid, (b) sulfurous acid, (c) a soluble sulfate, (d) an insoluble sulfate, (e) a sulfite.
9. Write the formula of (a) the sulfite, (b) the acid sulfite, (c) the sulfate, (d) the acid sulfate of NH_4 , Ca , Pb , Ag , Ba , Zn .

PROBLEMS

1. What weight of sulfur dioxide can be prepared from 25 gm. of sodium sulfite (92 per cent pure)?
2. How much sulfur (99 per cent pure) is needed to manufacture 100 tons of sulfuric acid containing 5 per cent of water?
3. A flask filled with water was found to weigh 72 gm., the flask alone weighing 22 gm. The flask filled with sulfuric acid weighed 114 gm. Calculate the specific gravity of the sulfuric acid.
4. What weight of pure sulfuric acid can be made from (a) 1000 tons of pure sulfur and (b) 1000 tons of pure FeS_2 ?

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

- Exercise *43 — Sulfur Dioxide (Short Method).
Exercise 44 — Sulfur Dioxide and Sulfurous Acid — T.
Exercise *45 — Properties of Sulfuric Acid.
Exercise *46 — Test for Sulfuric Acid, Sulfates, SO_4 -ions.

CHAPTER XIX

FUELS — ILLUMINANTS — PETROLEUM AND ITS PRODUCTS — DISTILLATION OF COAL — FLAMES

231. Carbon and energy. — When carbon and many of its compounds burn, the chemical energy is transformed in part into heat energy or light energy. Hence carbon and some of its compounds are **fuels and illuminants**.

232. Fuels and illuminants. — Fuels are substances which are burned to produce heat, *e.g.*, (a) wood, charcoal, coke, and coal, (b) petroleum, fuel oil, kerosene, and gasolene, and (c) natural, producer, water, and coal gases.

Illuminants are substances which are burned to produce light, *e.g.*, coal gas, oil gas, acetylene (gas), and kerosene.

233. Composition of fuels. — Wood is composed mainly of cellulose (a compound of carbon, hydrogen, and oxygen (§ 396)), water (10 to 50 per cent), and a small per cent of mineral matter. Charcoal and coke are nearly pure carbon (43, 44). Hard coal is about 90 per cent carbon, and soft coal about 70 per cent. All kinds of coal contain mineral matter, which is left as ashes when the coal is burned. Soft coal contains moisture and volatile matter.

Liquid fuels (except alcohol) are mixtures of hydrocarbons (compounds of hydrogen and carbon, § 246). Alcohol is a compound of carbon, hydrogen, and oxygen. The two common kinds of alcohol are ethyl alcohol or ethanol (C_2H_5OH) and methanol (CH_3OH). (See §§ 265, 266.)

Gaseous fuels contain hydrocarbons, hydrogen, and carbon monoxide; acetylene is a hydrocarbon (C_2H_2).

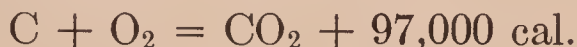
234. Combustion of fuels. — Fuels burn when heated to the proper temperature. Chemically this means that the carbon, hydrogen, and carbon monoxide (in the fuels) unite

with oxygen furnished by air. The gaseous products of combustion are carbon dioxide, carbon monoxide, and water. The solid products are the ashes and, if combustion is incomplete, smoke.

235. Measurement of heat produced by fuels. — The essential characteristic of a good fuel is its heat-producing capacity, especially when used to produce steam. Heat, like other forms of energy, is measured by a special unit. The unit used for fuels is the **British thermal unit** (B. t. u.). It is the amount of heat that will raise the temperature of 1 pound of water 1 degree measured on the Fahrenheit thermometer, or briefly 1 B. t. u. = 1 lb. water raised 1° F. The number of heat units produced by a given quantity of fuel, usually 1 pound or 1 cubic foot, is called its **fuel value**. Thus, coke yields about 14,300 B. t. u. per pound. Fuel oil, now extensively used in place of coal, yields about 18,500 B. t. u. per pound. Fuel gases (producer, water, and coal gas) give 145 to 600 B. t. u. per cubic foot.

Besides the British thermal unit, there is another heat unit called the **small calorie** (cal.). It is the amount of heat required to raise the temperature of 1 gram of water 1° C. (usually 15° to 16°). One B. t. u. equals 252 cal.

236. Thermo-chemical equations. — The heat liberated when carbon, or a carbon compound, burns can be incorporated in the equation expressing the chemical change. Thus, the thermo-chemical equation for the burning of carbon in the form of pure charcoal is: —



In this equation C stands for 12 gm. of carbon, O₂ for 32 of oxygen, CO₂ for 44 of carbon dioxide, and cal. for small calories.

237. Burning of coal. — Coal is the commonest fuel. Its fuel value varies with the kind and quality, *e.g.*, bituminous or soft coal yields from 9000 to 14,700 B. t. u. (or 8700 cal.) per pound and anthracite from 12,500 to 13,700.

When coal is burned, the products of combustion depend on the kind of coal and on the proportion of air supplied. With an excess of air, hard coal and good soft coal produce

carbon dioxide and water. If too much air is supplied, heat is also lost “up the chimney.” If the air is insufficient, carbon monoxide is formed, and some unburned carbon escapes as smoke, especially with soft coal.

The air needed for burning coal in stoves or under boilers is drawn in through an opening under the grate by the draft created by the gases as they rise up the chimney, though sometimes the air is forced in by a “blower.”

Both carbon dioxide and carbon monoxide are formed in a coal fire in a stove. When air enters the bottom of the grate (Fig. 90) and comes in contact with the burning coal, oxygen unites with carbon to form carbon dioxide. The carbon dioxide rises through the hot coal, and the carbon reduces the

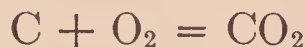
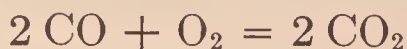
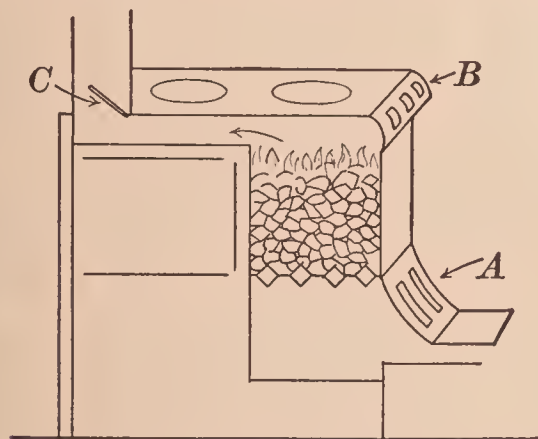


FIG. 90. — The three main changes during combustion in a coal fire.

carbon dioxide to carbon monoxide. Some of the carbon monoxide usually escapes, but most of it burns with a flickering bluish flame on the top of the fire, forming carbon dioxide with the oxygen of the air.

The combustion of coal in a stove or furnace in a house is regulated by dampers, usually three — a lower one in the door below the grate (A), a middle one in the door just above the fire (B), and an upper one in the pipe connected with the chimney (C) (Fig. 90).

When the fire is built, or needs to be “started up,” the dampers in the lower door and the pipe are opened but the one in the upper door is closed. This arrangement allows plenty of air to pass up through the burning coal and increase the combustion, and also creates a draft by permitting the hot products of combustion to rise and escape out of the chim-

ney. Once started, the combustion in the fire can be regulated by closing the lower damper and opening the middle one, partly or wholly, and adjusting the chimney damper; by this arrangement most of the air goes over the fire instead of up through it.

Care must be taken to admit enough air through the lower door to burn the coal as completely as possible, so that the maximum quantity of heat will be liberated. Special care should also be taken to prevent the escape of "coal gas" into the house. This gas contains carbon monoxide, which is poisonous (§ 62).

238. Burning other solid carbon fuels. — Charcoal burns with a slight flame, and yields no smoke. Its fuel value is 7000 to 8000 B. t. u. per pound. Coke also burns with a small flame and without smoke. Its fuel value is about 14,300 B. t. u. per pound. Both charcoal and coke find extensive use in the iron and steel industry (§§ 305, 312).

Wood has been used as a fuel for ages. The hard varieties such as oak, ash, and maple are the best fuels. Dry wood yields from 5600 to 8000 B. t. u. per pound.

239. Alcohol fuels. — Different kinds of alcohol are used as fuel, usually on a small scale. They burn without smoke and have a high fuel value. Methyl alcohol (CH_3OH), also called wood alcohol (§ 265) and methanol, gives about 9600 B. t. u. per pound. It is the fuel in "solid alcohol" (§ 265). Ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$), also called grain alcohol or simply alcohol, gives about 12,700 B. t. u. per pound.

240. Fuels from petroleum. — Three products from petroleum — fuel oil, gasolene, and kerosene — are used as fuels. They are mixtures of hydrocarbons (§ 246). In burning, these compounds are decomposed; the carbon forms carbon dioxide and the hydrogen forms water. They produce hot flames.

Fuel oil must be supplied to the furnace in the form of spray. This is produced by forcing the oil through a fine opening or by blowing it with steam or air through an atomizer. When the spray of oil burns, a large amount of heat is liberated, as high as 19,800 B. t. u. per pound in the case of some grades.

The general principle on which the latter type of burner operates is shown in Fig. 91. Oil enters at *A* and flows through *D* into the mixing and atomizing chamber *C*. Steam enters at *B* and passes through *F* and *E* into the chamber *C*, where it cuts across the oil at an angle. Here the oil and steam mix, and the pressure forces the oil as a fine spray out into the furnace, where it burns instantly with a hot flame.

Fuel oil is extensively used on warships and steamships, and in many manufactories. By using oil in place of coal to generate steam, additional space is provided for storage and more efficient combustion is attained.

Gasolene is the fuel used in the engines of automobiles, trucks, motor boats, motor cycles, airships, and airplanes.

Gasolene is very volatile and the vapor burns readily. If the vapor is mixed with air and the mixture is ignited by an electric spark, the combustion is so rapid that it is practically an explosion; the gases, suddenly expanded, exert pressure, which is converted by the machinery into steady and continuous motion.

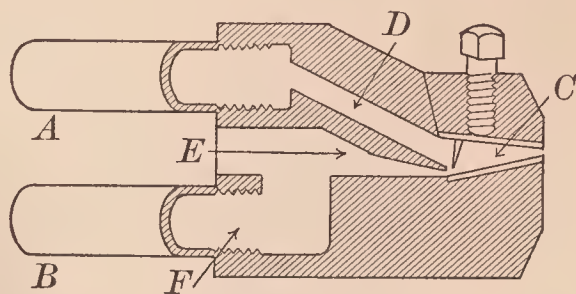


FIG. 91. — Fuel oil burner.

Kerosene is used as a fuel to a limited extent in engines and in cooking stoves. In some portable stoves kerosene is burned by means of a large wick (as in a lamp). The fuel value is sometimes as high as 19,900 B. t. u. per pound.

241. Petroleum and its products. — Petroleum is an oil which is distilled to obtain gasolene, kerosene, lubricating oil, vaseline, and paraffin. Its composition is complex, but all varieties are essentially mixtures of liquid and solid hydrocarbons (§ 246). Certain grades contain compounds of nitrogen and of sulfur.

In some localities the oil issues from the earth, but it is usually necessary to erect a derrick, drill a deep hole, and insert a pipe into the porous rock containing the oil. Sometimes the oil “spouts” out of the well when first drilled, but after a time a pump is usually needed to draw it to the surface.

The oil is forced by powerful pumps through large pipes

to central points for storage, or more often many miles to the refinery, where the petroleum is separated into various commercial products by refining.

242. Refining petroleum. — The petroleum is first cleaned by settling and filtration. Then it is distilled by heating it in huge retorts (Fig. 92), condensing the vapors in coiled pipes immersed in cold water, and collecting the distillates in separate tanks. This process is called **fractional distillation**. Certain products, *e.g.*, fuel oil, are obtained from the residue left in the stills (§ 244).

The different distillates are further separated and purified by redistillation (Fig. 92, top). The final products depend on the composition of the original petroleum and also on the demand for special commercial mixtures, *e.g.*, gasolene. The chief commercial liquid products are gasolene (boiling point 60° – 190° C.), kerosene (150° – 250° C.), fuel oil (250° – 350° C.) and various grades of lubricating oils (above 300° C.).

Formerly the gasolene fraction from ordinary distillation of petroleum met the limited need. The first step taken to increase the supply was **cracking**, *i.e.*, the higher boiling oils were vaporized and the vapor heated to a high temperature (350° – 450° C.) and under increased pressure (4 to 5 atmospheres). By this treatment, complex hydrocarbons decomposed and formed hydrocarbons within the gasolene range (§ 246). Another step was **blending**, *i.e.*, mixing the higher boiling hydrocarbons formerly sold as kerosene with “casing-head gasolene.” The latter contains chiefly the volatile hydrocarbons, pentane and hexane, and is obtained from natural gas by several methods, one of which is cooling and compressing the gas (to 15 to 20 atmospheres). The gasolene sold at present is usually blended and has a wide range of boiling point.

243. Kerosene. — This liquid is a mixture of hydrocarbons which have a higher boiling point than those in gasolene. Owing to its extensive use as an illuminant, crude kerosene is carefully freed from readily combustible liquids and gases, which might cause an explosion, and also from tarry matter and semi-solid hydrocarbons which would clog a wick. The purification is done by agitating the crude kerosene succes-

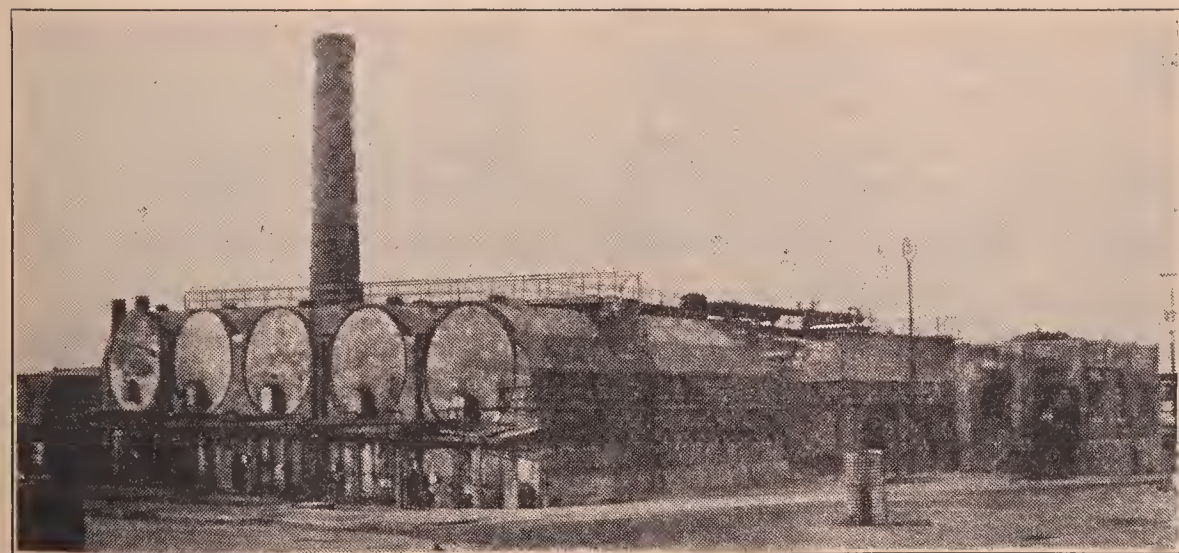
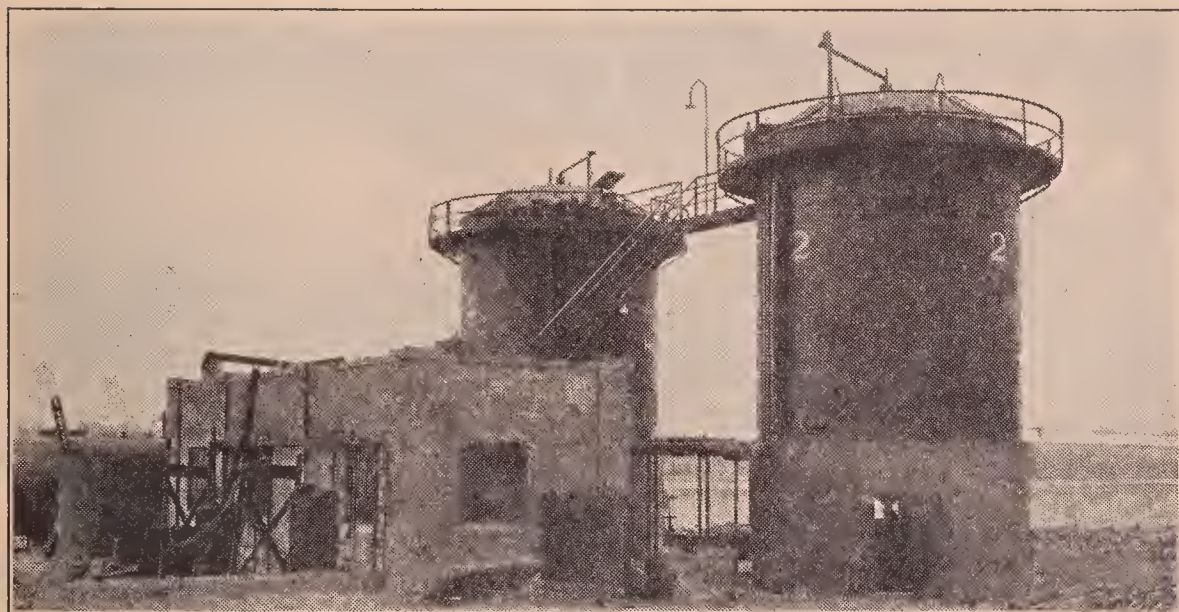
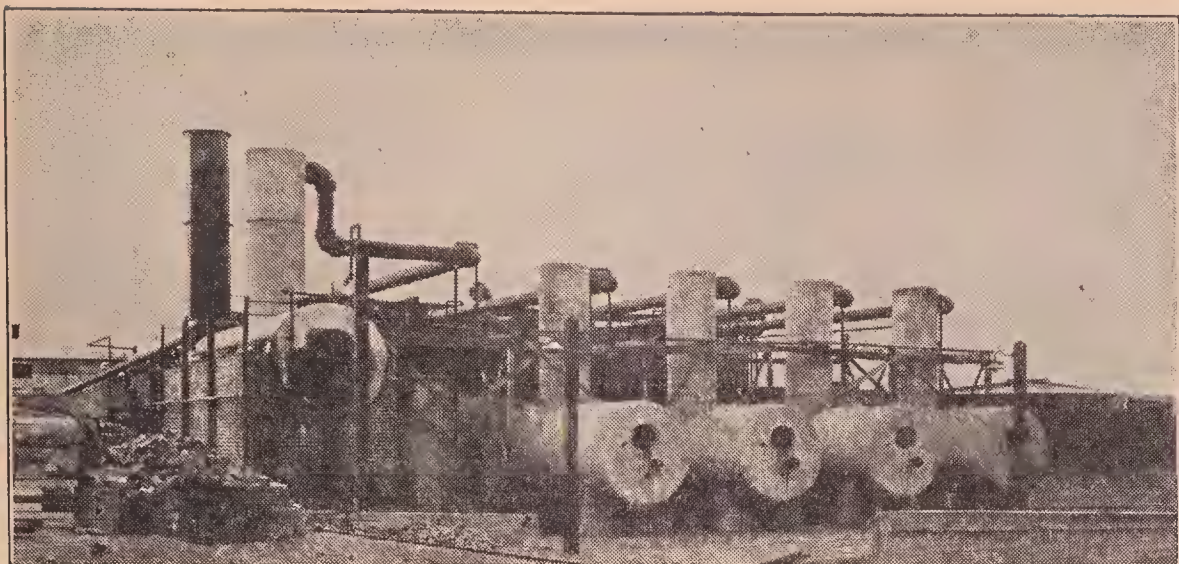


FIG. 92. — Refining petroleum. Fire stills (bottom), steam stills (top), agitators (middle).

sively with sulfuric acid, sodium hydroxide, and water (Fig. 92, middle).

Commercial kerosene must have a **legal flashing point**. This is "the temperature at which the oil gives off sufficient vapor to form a momentary flash when a small flame is brought near its surface." The legal minimum flashing point in most states is about 110° Fahrenheit (about 44° C.).

244. Fuel oil and other products. — The oil left in the fire still (Fig. 92, bottom) after the removal of the low-boiling liquids including gasolene, and sometimes kerosene, is **fuel oil**.

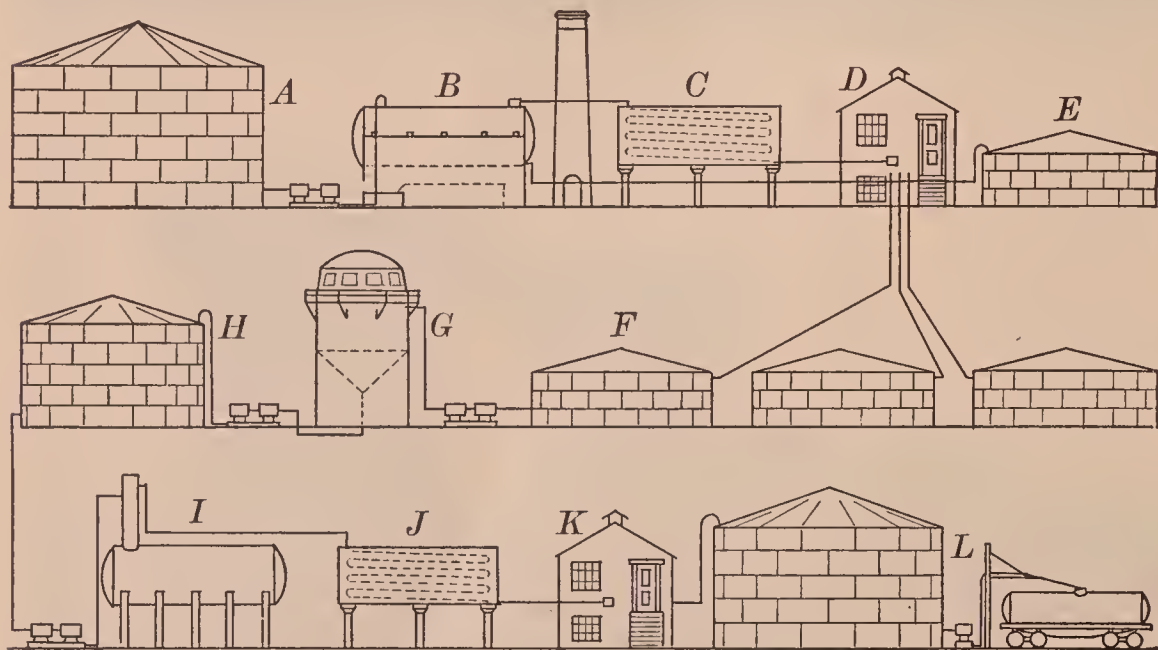


FIG. 93. — Sketch of a plant for the separation of gasolene and fuel oil from petroleum.

Other oil residues, and crude petroleum itself, are also used as fuels under the name fuel oil. Specifications usually prescribe the properties of the fuel oil required, especially its heating value, freedom from water and from sulfur compounds, and mobility.

From the residue after the distillation of the kerosene many grades of **lubricating oil** are obtained; also **vaseline** and **paraffin wax**. Petroleum oils yielding these products are said to have a paraffin base; Pennsylvania and Ohio oils are examples. Vaseline finds extensive use as an ointment. Paraffin wax is made into candles and into a water-proof coating for many substances. The final residue in

the still is mainly carbon and is called **petroleum coke**; it is made into electric light carbons.

Some oils, such as those from Mexico and California, leave a thick, black pitch. These oils are said to have an asphalt base.

245. Separation of fuel oil and gasolene from petroleum. — The steps in the separation of gasolene and fuel oil from petroleum are shown in Fig. 93. This figure also illustrates the general process of refining. The crude oil is pumped from the storage tank *A* into the still *B* (Fig. 92, bottom), which is heated on the bottom by a flame. The vapors pass into the condenser *C*, and the distillate flows into the receiving house *D*, where it is examined through look boxes. The different portions (called fractions) are run into the proper tank. After certain low-boiling hydrocarbons (making up gasolene and kerosene chiefly) have been boiled off in the fire still, the residue is drawn off and stored in the fuel oil tank *E*. The benzine fraction *F* is pumped to the agitator *G* (Fig. 92, middle) and then to the storage tank *H*. From here the liquid goes to the still *I*, which is heated by steam (Fig. 92, top). The vapors are condensed in *J*, the distillate received in *K*, examined, and directed into the proper tank — the main one being the gasolene tank *L*.

246. Hydrocarbons. — These are compounds of hydrogen and carbon. They occur as gases, liquids, and solids. Over two hundred and fifty are known. Many are found in petroleum, natural gas, asphalt, and coal tar. Hydrocarbons are divided into series according to their composition. The commonest series is the **methane or paraffin series**. The first members in order are methane (CH_4), ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), pentane (C_5H_{12}), and hexane (C_6H_{14}).

Petroleum is a mixture of many hydrocarbons, and most American varieties consist largely of paraffin hydrocarbons. Gasolene is mainly a mixture of hexane (C_6H_{14}), heptane (C_7H_{16}), and octane (C_8H_{18}). Kerosene consists of hydrocarbons which are composed of ten to sixteen carbon atoms, vaseline twenty-two and twenty-three, and paraffin wax still higher.

247. Gaseous fuels. — These include natural gas and the various mixtures obtained from coal, *e.g.*, producer gas (§§ 65, 385), water gas (§§ 65, 386, 387), and coal gas.

Natural gas exists in the earth in Pennsylvania, Ohio,

West Virginia, and other parts of the United States, usually in regions where petroleum is found. It contains from 90 to 98 per cent methane (CH_4), which is the chief heat-producing constituent. Natural gas burns with a hot flame. The fuel value is about 1000 B. t. u. per cubic foot. It is used as a fuel to heat houses and to generate steam in many industries, *e.g.*, making steel, glass, brick, and pottery.

248. Coal gas. — This is made by dry or destructive distillation of coal, *i.e.*, by heating coal to a high temperature in closed retorts. The volatile product (§ 250) is largely a mixture of hydrogen (45 to 50 per cent) and methane (30 to 36 per cent); other ingredients are hydrocarbons (ethylene, etc.), carbon monoxide (6 per cent) and dioxide, and nitrogen. It burns with a yellow flame.

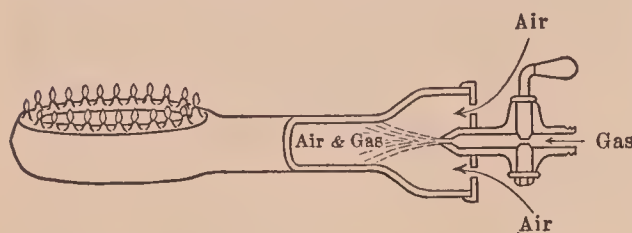


FIG. 94. — A gas range burner.

able air is admitted and a special burner is used. In the laboratory we use the Bunsen burner (§ 252). In houses the gas range burner is merely several small modified Bunsen

burners arranged advantageously (Fig. 94). The fuel value of coal gas varies from 525 to 600 B. t. u. per cubic foot.

249. Illuminants. — Some of the gases used as fuel are also used as a source of light, *i.e.*, as illuminants. Coal gas and enriched water gas are the most important (§§ 65, 386, 387).

250. Manufacture of coal gas. — Coal is subjected to dry distillation to prepare coal, or illuminating, gas. The gas is used as a fuel, *e.g.*, in a kitchen gas range, and also as an illuminant.

The manufacture of coal gas can be understood from the diagram of a coal gas plant shown in Fig. 95. (1) The coal is heated externally for several hours in closed retorts (*A*). The volatile products escape from the retorts and bubble through water into a large iron pipe called the **hydraulic main** (*B*). Here some of the tar is deposited and ammonium compounds are dissolved by the water which flows constantly through the main and prevents the gas from escaping back into the retorts. The ammoniacal liquor and tar flow into the tar well (*C*).

(2) From the hydraulic main the hot and impure gas passes through

vertical pipes called the condenser (*D*), which cools the gas and removes tar.

(3) An exhaustor (*E*) draws or forces the gas from the condenser into the scrubber (and onward through the purifiers into the gas holder).

(4) The scrubber (*F*) is a tall tower filled with coke or pebbles over which ammoniacal liquor and water trickle. The object of the scrubber is to remove the remaining ammonium compounds, and also carbon dioxide, hydrogen sulfide, and the last traces of tar.

(5) From the scrubber the gas passes into the purifier (*G*), which is a series of shallow rectangular boxes fitted with frames loosely covered with lime or hydrated ferric oxide, or both. In the purifier the remaining carbon dioxide and sulfur compounds are removed.

(6) The purified gas next passes through a large meter, which records its volume, and then into a gas holder (*H*), where it is stored over water and finally forced through pipes to the consumer.

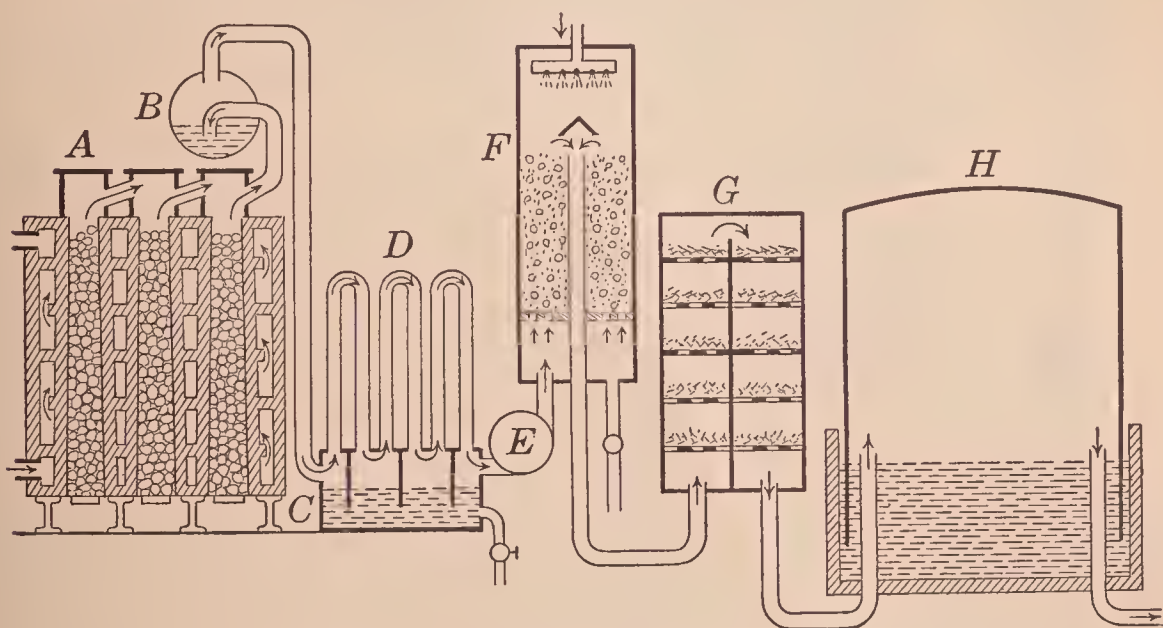


FIG. 95. — Diagram of coal gas plant.

A ton of good gas coal yields about 10,000 cubic feet of gas, 1400 pounds of coke (§ 44), 120 pounds of tar, 20 gallons of ammoniacal liquor (§ 189), and a varying amount of gas carbon (§ 45).

The tar, or **coal tar** as it is often called, collected from the hydraulic main and condenser, is a thick, black, foul-smelling liquid. Some is used for preserving timber, making road material, tarred paper, and black varnishes, and as a protective paint. Most of it is separated by distillation into its important constituents. Among these are the hydrocarbons benzene (C_6H_6), toluene (C_7H_8), naphthalene ($C_{10}H_8$), and

anthracene ($C_{14}H_{10}$). They are indispensable substances, being the parent substances of dyes, medicines, photographic chemicals, and explosives. Naphthalene is sometimes called moth balls and is used as a substitute for camphor. Among other products from coal tar are creosote oils and carbolic acid (phenol, C_6H_5OH), which are useful disinfectants.

251. Illuminating gas. — Coal gas is often burned alone but water gas is usually mixed with 60 or 70 per cent of coal gas. This mixture is called “illuminating gas.” Owing to the high percentage of carbon monoxide, water gas and mixtures containing it are poisonous (§ 62).

Illuminating gases are mixtures of varying proportions. Table VI shows the approximate composition.

Methane, hydrogen, and carbon monoxide burn with a feeble (non-yellow) flame; they furnish heat, but little light. The illuminants consist of ethylene (C_2H_4), acetylene (C_2H_2), benzene (C_6H_6), and other hydrocarbons. The illuminants furnish the carbon particles which give the flame its yellow color.

252. The Bunsen burner and its flame. — When a mixture of air and illuminating gas is burned in a suitable burner, a flame is produced

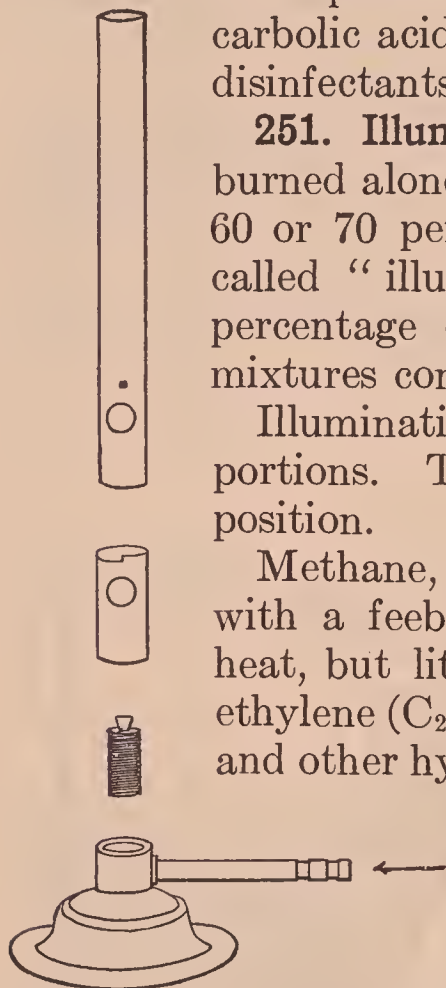


FIG. 96. — Parts of a typical Bunsen burner.

TABLE VI. — COMPOSITION OF ILLUMINATING GASES

CONSTITUENTS	COAL GAS	WATER GAS	MIXED GAS
Methane	34.44	15.23	29.81
Illuminants	4.17	11.07	6.38
Hydrogen	50.31	35.04	46.51
Carbon Monoxide	6.60	33.42	12.02
Carbon Dioxide	0.81	2.66	1.78
Nitrogen	3.67	2.24	3.28
Oxygen	0.00	0.34	0.22

which is non-luminous and hot, and deposits on carbon. Such a flame is called the **Bunsen flame**. It was first produced in a burner devised by the German chemist Bunsen. This burner is used in laboratories as a source of heat. The parts of a typical burner are shown in Fig. 96.

The gas enters the base and flows from a small opening into the long tube, which screws down over this opening. At the lower end of the tube and above the inlet are two holes, through which air is drawn by the gas as it rushes out of the small opening. The gas and air mix as they rise in the tube, and the mixture burns at the top of the long tube.

The size of the air holes at the bottom can be changed by a movable ring. When the holes are wide open, the typical non-luminous Bunsen flame is formed; this flame is free from soot, and apparatus heated by it is not blackened. When the holes are closed, the gas burns with a luminous flame and deposits carbon.

The gas burns at the top of the tube and not inside, because the proper mixture of gas and air rushes out more quickly than the flame can travel back through the tube to the small inlet. If the gas supply is slowly decreased, the flame becomes smaller, disappears down the tube with a slight explosion ("strikes back"), and burns at the small gas inlet inside the tube. A sudden draft of air, too much air admitted through the holes at the lower end of the tube, or too low gas pressure may cause the flame to "strike back."

This modified flame, which has a pale color, a disagreeable odor, and deposits soot, should be extinguished and the proper flame produced before further use.

The Bunsen flame (Fig. 97) consists essentially of two cones, which may often be distinguished by the different tints. The lower and inner cone consists of air and unburned gas. It is bluish, but becomes green when too much air is admitted (best seen in an imperfect flame). The outer cone is the flame proper and consists of burning gases. It is faint blue and hot (about 1500°C.).

The *inner* cone consists of unburned gases. This can be shown by putting one end of a small bore glass tube into the cone; gas will rise

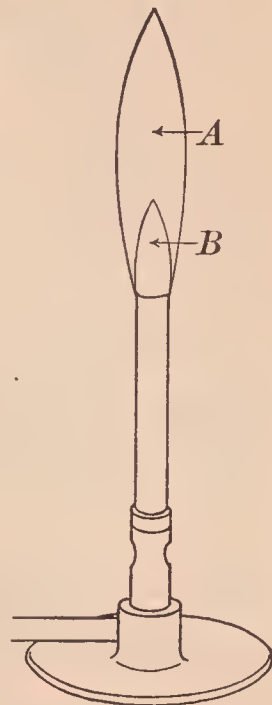


FIG. 97. — Sketch of a Bunsen flame.

through the tube and can be ignited at the upper end (Fig. 98, left). If a match is supported by a pin across the top of an unlighted burner, it will not become ignited until some time after the gas is first lighted (Fig. 98, center).

The *outer cone* consists of burning gases. Thus, a match held near the flame ignites quickly, while a match laid for an instant across the top of the tube is charred only at the two points where it touches the outer cone.

Finally, a wire gauze, if pressed down upon the flame, shows a dark disk surrounded by a luminous ring due to the inner and outer cone respectively (Fig. 98, right).

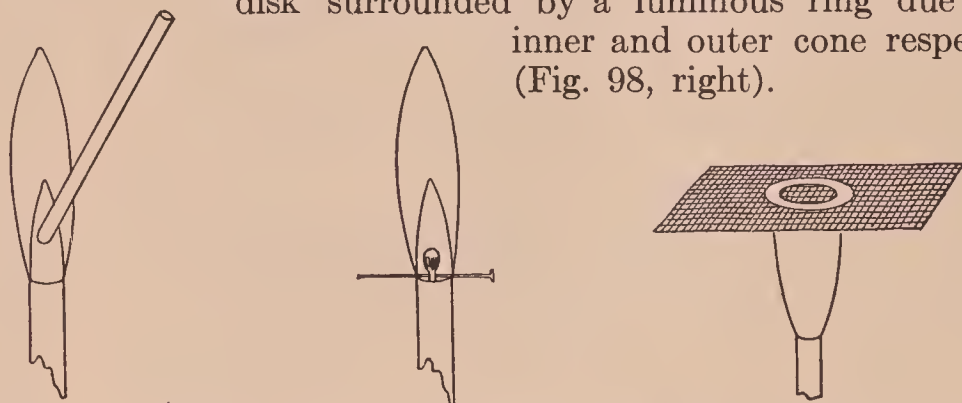


FIG. 98. — The cones of a Bunsen flame. Drawing unburned gases from the inner cone (left). A match does not ignite in the inner cone (center). The inner cone produces a dark disk and the outer cone a luminous ring (right).

253. Oxidizing and reducing flames. — The outer portion of the Bunsen flame is the **oxidizing flame**. The inner and

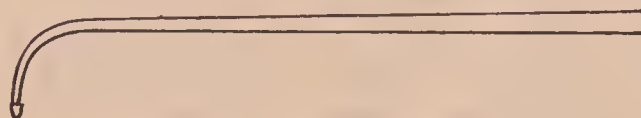


FIG. 99. — A mouth blowpipe.

lower portion is the **reducing flame**. A sketch of these flames is shown in Fig. 97. *A* is the most effective part of the oxi-

dizing flame, and *B* of the reducing flame. At *A* metals are oxidized, and at *B* oxygen compounds are reduced.

Sometimes the oxidizing and reducing flames are produced by a mouth blowpipe (Fig. 99). A special tube with a flattened top is put inside the burner tube to produce a luminous flame, and the tip of the blowpipe is put in or very near this flame. If air is gently and continuously blown through the blowpipe, a long slender flame is produced, called a blowpipe flame (Fig. 100).

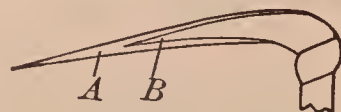


FIG. 100. — A blowpipe flame. *A* is the oxidizing part and *B* is the reducing part.

EXERCISES

1. What is the fuel value of (a) hard coal, (b) fuel oil, (c) coke?
2. Define and illustrate a thermal equation.
3. Prepare a summary of (a) burning coal, (b) manufacturing coal gas, (c) fuel oil.
4. Explain the use of gasolene in an automobile.
5. Prepare an outline of the process of refining petroleum.
6. Complete: (a) $C + \text{---} = CO$; (b) $CO + \text{---} = CO_2$;
(c) $CO_2 + \text{---} = CO$.
7. Draw a diagram of the apparatus for manufacturing coal gas.

PROBLEMS

1. A candle weighing 50 gm. consists of wax composed of 88 per cent carbon and 12 per cent hydrogen. What weight of (a) carbon dioxide and of (b) water will be formed by burning half the candle?
2. What volume of air (containing 21 per cent of oxygen by volume) will be required for the combustion of 100 tons of coal, assuming that the coal is 80 per cent pure carbon and burns to carbon dioxide?
3. Ten tons of coke were burned and only 35 tons of carbon dioxide were produced. Calculate the per cent of carbon in the coke.

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

- Exercise *48 — Distillation of Soft Coal.
Exercise *49 — Distillation of Wood — T.
Exercise *50 — Illuminating Gas Flame — T.
Exercise *51 — Candle Flame — T.
Exercise *52 — Bunsen Burner Flame — T.
Exercise *53 — Reduction and Oxidation with the Blowpipe.
Exercise S39 — Carbonic Acid — T.
Exercise S40 — Acetylene — T.

SUPPLEMENTARY SECTIONS FROM PART II

383. Measurement of fuel value.
384. The calorimeter is used to find fuel value.
385. Producer gas.
386. Water gas.
387. Manufacture of water gas.
388. The illuminating gas flame.
389. Other luminous flames.
390. The candle flame.
391. Acetylene and its flame.
392. The oxy-acetylene flame.

CHAPTER XX

SUGAR—STARCH—ACETIC ACID—METHANOL— ETHYL ALCOHOL

254. Sugars. — The most important sugars are (1) ordinary sugar, also called cane sugar and sucrose, (2) dextrose or glucose, (3) levulose or fruit sugar, (4) lactose or milk sugar, and (5) maltose.

255. Sucrose. — Sugar cane contains about 18 per cent and sugar beets from 12 to 15 per cent; these are the main sources of sucrose.

Sucrose is a white solid. It is very soluble in water; one part of water dissolves about three times its weight of sugar at ordinary temperatures. If sugar is carefully heated, it melts. As the temperature is raised, the sugar begins to decompose, water is given off, and a light brown substance called **caramel** is formed which is used to color soups, gravies, and beverages. By further heating, a black porous mass of carbon is finally obtained, often called **sugar charcoal**. Thus we see that sucrose consists of carbon, hydrogen, and oxygen. Its formula is $C_{12}H_{22}O_{11}$.

If sucrose is boiled with very dilute acid, it undergoes hydrolysis, *i.e.*, it interacts with water. By this reaction a mixture of dextrose and levulose is formed, which is called **invert sugar**.

Sugar is extracted from sugar cane or sugar beet by treating with water and purifying substances, and evaporating the solution until the sugar will crystallize. The crystals are separated by machinery, and molasses is left. The raw sugar, as it is called, is refined, *i.e.*, purified and crystallized. One important step in the purification is the removal of coloring matter by passing the straw-colored solution through a deep layer of animal charcoal (§ 43).

256. Dextrose. — This sugar is about three fifths as sweet as sucrose. It is very soluble in water. Dextrose is found in honey and in many fruits, especially grapes, and is sometimes called **grape sugar**. Another name for it is **glucose**.

Dextrose ferments with ordinary yeast, thus



Dextrose is an inexpensive substitute for sucrose, and is extensively used in making candy, jellies, and sirups.

257. Levulose. — This sugar is found in fruits and honey, and is often associated with dextrose. It is sometimes called **fructose** or **fruit sugar**.

258. Testing for dextrose. — Dextrose and levulose are reducing agents, and are called reducing sugars. An alkaline solution of dextrose is sometimes used to reduce a silver solution and deposit the silver as a bright film in making reflectors for automobiles, mirrors, radio tubes, and thermos bottles. Dextrose reduces an alkaline solution of copper sulfate and sodium potassium tartrate (or sodium citrate), known as Fehling's solution. Thus, when this solution is boiled with dextrose (or any reducing sugar), a reddish, insoluble copper compound (cuprous oxide, Cu_2O) is formed. This method is often used as a **test for reducing sugar**.

259. Lactose. — This sugar occurs in milk and is sometimes called **milk sugar**. Cow's milk contains from 3 to 5 per cent of lactose. Lactose is not so sweet or soluble as sucrose. A solution of lactose reduces Fehling's solution.

Lactose is not fermented by ordinary yeast, but a special ferment, called lactic ferment, converts it into alcohol and lactic acid. The lactic acid gives milk its sour taste and also assists in curdling the milk, *i.e.*, in changing the casein into a clot or curd. Lactose is obtained from whey. This is the liquid left after the solids have been pressed from milk which has been curdled by rennet in the manufacture of cheese. Lactose is used in infant foods and certain medicines.

260. Maltose. — This sugar is formed from starch by malt. The transformation is caused by diastase, which is formed in the malt by allowing moist barley to sprout in a

warm place. Maltose is also formed from starch by the ptyalin in the saliva when food is well chewed.

Maltose ferments readily with yeast, forming first dextrose and ultimately alcohol and carbon dioxide. Maltose reduces Fehling's solution.

261. Starch. — This substance is found in wheat, corn, and all other grains, in potatoes, beans, peas, and similar vegetables, and also in rice, sago, tapioca, and nuts (especially the chestnut). Many parts of plants contain starch, especially the root, seed, and fruit.

The food value of vegetables depends largely on the starch they contain. Large quantities of starch are consumed as food, and in the manufacture of glucose and adhesives.

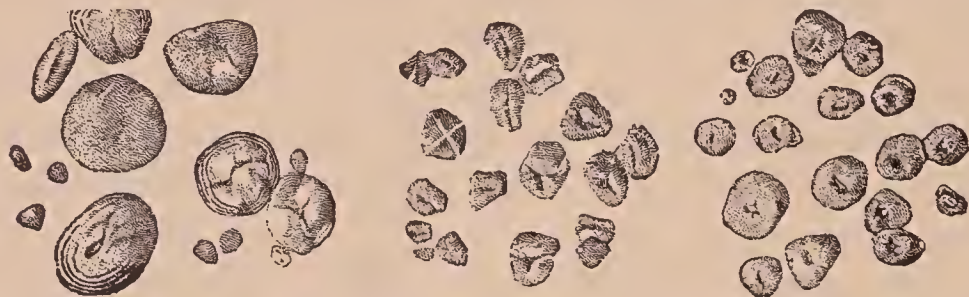


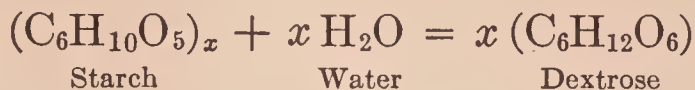
FIG. 101. — Starch grains (magnified) — wheat (left), rice (center), corn (right).

Starch, as usually seen, is a white, compact mass, but it really consists of granules which differ in size and shape with the plant (Fig. 101).

Starch is not soluble in water. The granules are enveloped in an insoluble membrane of cellulose (§ 396). But if the starch is boiled with water, the membrane softens, the swollen grains burst through the membrane and form a clear liquid with the water. If a little water is used, a jelly-like mass is produced — the familiar starch paste. With cold water, starch forms an ordinary suspension. Whereas with considerable hot water, a colloidal suspension is produced, *i.e.*, the particles are exceedingly small and do not settle (§ 95).

Starch gives a blue colored substance when added to dilute iodine solution. The presence of starch in many vegetables and foods can be readily shown by grinding the substance in a mortar with cold water and adding a drop of dilute iodine solution. Starch does not reduce Fehling's solution.

Starch is a complex compound and its composition corresponds to the formula $(C_6H_{10}O_5)_x$. Starch is readily transformed into maltose by the ptyalin in the saliva. With dilute acids starch undergoes hydrolysis, thus:—



262. Making bread.—Wheat flour contains about 70 per cent of starch. The remainder is chiefly water and gluten. In making bread, the flour, water, fat, sugar, and yeast are thoroughly mixed into dough, which is put in a warm place to rise. Fermentation begins at once. Fermentation is the conversion of an organic compound, like starch or some sugars, into simpler compounds by the action of enzymes, *e.g.*, diastase and ptyalin.

By fermentation in the dough, alcohol and carbon dioxide are formed. The gases escape in part through the dough, which becomes light and porous. When the dough is baked, the heat stops the action of the enzymes; but the alcohol, carbon dioxide, and some water escape and puff up the mass still more. The heat, however, soon hardens the starch, gluten, etc., into a firm, porous loaf.

263. Destructive distillation of wood.—Wood is composed essentially of cellulose (§ 396) and related organic compounds,

water, and mineral matter. Cellulose is a compound of carbon, hydrogen, and oxygen. When wood is heated in large iron furnaces from which air is excluded, the cellulose and the other organic compounds decompose. In the laboratory a simple apparatus may be used (Fig. 102). Volatile

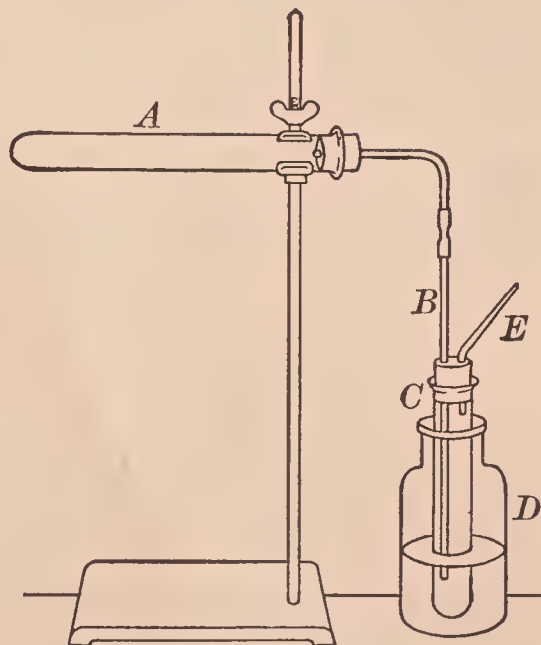


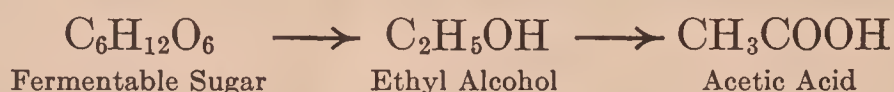
FIG. 102. — Laboratory apparatus for the destructive distillation of wood. Wood is put in *A* and heated. The volatile products condense in *C*, charcoal is left in *A*, and gaseous products may be burned at *E*.

products distill over with the water, and about thirty per cent of the wood remains in the furnace as wood charcoal (§ 43). This process is called dry or **destructive distillation** to distinguish it from ordinary distillation (§ 82). The distillate is a brown liquid called pyroligneous acid. It contains acetic acid (about 10 per cent) and methanol.

264. Acetic acid. — The acetic acid (CH_3COOH) in the wood distillate is obtained by neutralizing the distillate with lime, decomposing the calcium acetate thereby formed, and distilling off the liberated acetic acid.

Ordinary commercial acetic acid contains about thirty per cent of the acid, whereas **glacial acetic acid** is very concentrated — nearly 100 per cent acid.

Vinegar contains from 4 to 6 per cent of acetic acid. It is prepared by the transformation of sugars into ethyl alcohol, which is then changed into acetic acid by oxidation (through the action of bacteria). Substances containing fermentable sugars (§ 256), *e.g.*, fruit juices, cider, and molasses, ferment slowly when exposed to the air, which always contains bacteria, and the ethyl alcohol becomes acetic acid, thus: —



Acetic acid is a weak acid (§ 185). It forms many useful salts, *e.g.*, sodium acetate (CH_3COONa), lead acetate ($(\text{CH}_3\text{COO})_2\text{Pb}$), and Paris green. The last named is a complex compound containing arsenic and copper and is used to kill potato bugs and other insect pests (§ 415).

A **test for acetic acid** is the formation of ethyl acetate by interaction with ethyl alcohol. If a few drops of concentrated sulfuric acid are added to a mixture of acetic acid and ethyl alcohol, and the whole warmed gently, a pleasant fruitlike odor is detected. This is due to ethyl acetate which belongs to a class of compounds called **esters** (Pt. II, § 395).

265. Methanol. — This is an alcohol and was formerly called “wood alcohol.” It is used as a fuel, being the alcohol in “solid alcohol” (not solidified alcohol, but a mixture of methanol and a non-combustible gelatinous substance). Large quantities are used as a solvent for shellac gum; the

odor of the liquid called “shellac” is due to methanol. Some methanol is used to prepare denatured alcohol (§ 266). Methanol is a dangerous poison.

Methanol is now largely manufactured by a synthetic process, which is much cheaper than the older process of distilling wood. A mixture of carbon monoxide and hydrogen at a high pressure and temperature is passed over a suitable catalyst. The equation is: —

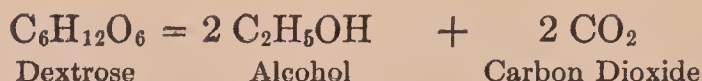


266. Alcohols. — These are compounds of carbon, hydrogen, and oxygen. There are many alcohols. One — methanol or methyl alcohol — has just been described (§ 265). The other important one is **ethyl alcohol** (sometimes called by the old name grain alcohol or the new name ethanol). Ethyl alcohol has the formula $\text{C}_2\text{H}_5\text{OH}$.

Ordinary commercial ethyl alcohol contains 4 to 5 per cent of water. **Absolute alcohol** is 100 per cent ethyl alcohol. **Denatured alcohol** is essentially a mixture of 100 parts ethyl alcohol, 10 parts methanol, and a small proportion of some poisonous, or unpalatable, substance, such as benzene, pyridine, or kerosene. (There are many legal recipes for preparing specially denatured alcohol.) Denatured alcohol is not suitable for use as a beverage, but specially denatured kinds can be used for industrial processes.

Ethyl alcohol is used in manufacturing varnishes, celluloid, collodion, rayon (artificial silk), extracts, perfumes, dyes, ether ($(\text{C}_2\text{H}_5)_2\text{O}$), chloroform (CHCl_3), iodoform (CHI_3), and numberless other organic compounds. It is indispensable in many industries.

Ethyl alcohol is manufactured either by the fermentation of the sugar left in the molasses, which remains from the extraction of crystallizable sugar in the sugar cane, or from vegetables and grains containing much starch, *e.g.*, potatoes and corn. If starch is used, it must be first changed into a fermentable sugar by treatment with an enzyme called diastase which is obtained from sprouting barley (malt). Yeast is added to the molasses or the sugar and an enzyme (zymase) in the yeast converts the sugar into alcohol and carbon dioxide. An equation is: —



A test for ethyl alcohol is the formation of ethyl acetate (see end of § 264).

EXERCISES

1. State the properties of sucrose.
2. Compare dextrose and levulose. How are these sugars related to sucrose?
3. What is the test for dextrose and similar sugars?
4. Define and illustrate by means of sugars (a) hydrolysis and (b) fermentation.
5. How would you show that a leaf contains starch?
6. How is acetic acid made?
7. What is (a) methanol, (b) ethanol?

PROBLEMS

(See Problems at the end of Chapters VIII and IX.)

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

Exercise 54 — Sugars

Exercise 55 — Starch.

Exercise *49 — Distillation of Wood — T.

Exercise S41 (a) — Esters (Test for Acetic Acid).

Exercise S41 (a) — Esters (Test for Ethyl Alcohol).

SUPPLEMENTARY SECTIONS FROM PART II

393. Manufacture of soap.
394. The cleansing action of soap.
395. What is soap?
396. Cellulose.
397. Derivatives of cellulose.
398. Paper.

At this point selections may be made from the sections in Topics XVII (Food and Nutrition), XVIII (Phosphorus — Arsenic Insecticides — Alloys of Antimony and Bismuth), XIX (Arrangement of the Elements by Atomic Weights and by Atomic Numbers), XX (Fluorine — Bromine — Iodine), XXI (Silicon Dioxide — Silicates — Silicon Carbide — Silicon Tetrafluoride — Glass).

CHAPTER XXI

METALS IN GENERAL

267. Metals and non-metals. — The elements are often divided into metals and non-metals. The division is based largely on the conspicuous physical properties of the elements. Thus, the opaque, lustrous, more or less heavy, hard, ductile, malleable, tenacious solids are called **metals**. Whereas, all elementary gases, the liquid bromine, and solids such as carbon, sulfur, phosphorus, and iodine are called **non-metals**.

A few elements sometimes act as metals and at other times as non-metals. Aluminum and antimony belong to this border-line class.

Table VII shows the metals and non-metals in their usual class. The elements that may be in both classes are inclosed in a parenthesis.

TABLE VII. — METALS AND NON-METALS

METALS			NON-METALS	
Sodium	Magnesium	—	Hydrogen	Oxygen
Potassium	Zinc	Chromium	—	Sulfur
—	—	—	Boron	—
Copper	Mercury	Manganese	—	Fluorine
Silver	—	—	Carbon	Chlorine
Gold	Aluminum	Iron	Silicon	Bromine
—	—	Cobalt	—	Iodine
Calcium	Tin	Nickel	Nitrogen	—
Strontium	Lead	—	Phosphorus	(Aluminum)
Barium	(Arsenic)	Platinum	Arsenic	—
	Antimony		(Antimony)	(Tin)
	Bismuth			(Chromium)
				(Manganese)

268. Occurrence of metals. — Only a few metals are found in the native, or free, state in the earth's crust, the important ones being gold, silver, copper, and platinum.

Most of the metals occur in the earth's crust as compounds, which are often called **minerals**. And the minerals from which metals can be profitably extracted are called **ores**.

The most abundant classes of metal compounds are oxides, sulfides, and carbonates; other classes are chlorides, sulfates, phosphates, and silicates. Many ores contain arsenic.

269. Properties of metals. — All have a **metallic luster**, *i.e.*, the marked property of reflecting light from their polished or untarnished surfaces. All are **opaque** except in very thin films.

The **color** of many is white (silvery), though the tint varies. Thus, silver, sodium, aluminum, mercury, magnesium, iron, and tin are nearly pure white; bismuth is reddish white. Copper is the only red metal, and gold the only yellow one, which are elements.

Most metals are **malleable** and **ductile**, *i.e.*, they may be hammered or rolled into sheets and drawn into wire. Gold, copper, silver, iron, platinum, and aluminum possess both these properties (malleability and ductility) to a marked degree; while lead, zinc, and tin are very malleable though not so ductile. Antimony and bismuth are **brittle**.

The **hardness** of metals varies. At ordinary temperatures sodium and lead can be cut easily with a knife, and so on through the list up to iridium, which is as hard as steel.

In **specific gravity** (*i.e.*, weight compared with the weight of an equal volume of water), the metals range between lithium, which is about 0.5, and osmium 22.5. Sodium and potassium are lighter than water, while magnesium has the specific gravity 1.75, and aluminum 2.58.

Metals are good **conductors** of heat and electricity. They vary in this property. Silver, copper, and aluminum are the best conductors, and have therefore many practical applications, especially copper.

Several of the distinctive chemical properties of metals already have been studied.

1. Many metals form oxides when exposed to air or heated in oxygen. Iron is a conspicuous example.

2. Metallic oxides dissolve in water and produce bases, *e.g.*, calcium oxide (CaO) and water form calcium hydroxide (Ca(OH)_2).

3. Certain metals react with water. Some, like sodium, react with cold water, others, like calcium, with hot water, and still others, like iron, magnesium, and zinc, with steam. Hydrogen is always produced together with an oxide or hydroxide.

4. Certain metals react with acids, *i.e.*, they displace hydrogen from acids and produce salts. (Nitric acid behaves exceptionally, § 203.) Not all metals displace hydrogen from acids; hence we have a displacement series divided by hydrogen (see § 72 and 6 below).

5. Metals form cations — positively charged ions — when salts are dissolved in water (§ 171), and in the electrolysis of salts metallic ions migrate to the cathode where they become atoms which (1) are deposited as metals, *e.g.*, copper or (2) interact with water and form secondary products, *e.g.*, sodium forms hydrogen and sodium hydroxide (§ 181).

6. Metals displace other metals, as well as hydrogen, from solutions. They vary in their displacing power and can be arranged in a displacement (or electromotive) series based on this power. Magnesium is at one end, gold at the other, and hydrogen about midway (§§ 72, 462), thus: Magnesium, aluminum, zinc, iron, lead, hydrogen, copper, mercury, silver, gold.

270. Extraction of metals. — The series of operations by which metals are extracted from their ores and prepared for manufacture into useful articles is called **metallurgy**. Typical processes are fully described in the chapter on iron and in the topics devoted to copper, aluminum, zinc, and lead.

271. Alloys. — The term *metallurgy* also includes the preparation of alloys. These are mixtures, or compounds, of two or more metals. Some fused metals mix in all proportions, while others seem to form definite compounds. Alloys look like metals, indeed certain alloys, *e.g.*, some of gold, can hardly be distinguished from the pure metal. The properties of alloys vary with the constituents and their proportions. Some alloys have many industrial uses. For example, iron alloys (§ 315) are indispensable in automobiles, crushing machinery, and tools; copper alloys, known as brass and bronze, are widely used; and the aluminum alloy called duralumin is made into articles which range from kitchen ware to airships. Alloys in which mercury is a constituent are called **amalgams**.

EXERCISES

1. Define (a) metallic luster, (b) malleable, (c) ductile, (d) specific gravity.
2. Name four distinctive (a) physical and (b) chemical properties of metals.
3. Define and illustrate (a) mineral and (b) ore.
4. What are (a) alloys, (b) amalgams? Illustrate each.

PROBLEMS

(See Problems at the end of Chapters VIII and IX.)

1. What is the specific gravity of gold, if a piece weighs 4.676 gm. in air, and loses 0.244 gm. when weighed in water?
(Note: Specific gravity equals the weight in air divided by the loss of weight in water.)
2. A piece of aluminum weighs 150 gm. in air and 75 gm. in water. What is its specific gravity?
3. A piece of iron weighs 292.8 gm. in air and 255.3 gm. in water. What is its specific gravity?

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

- Exercise *61 — Displacement of Metals.
- Exercise 62 — Flame Tests for Metals.
- Exercise S56 — Tests for Metals.
- Exercise S57 — Tests with Borax Beads.
- Exercise S58 — Cobalt Nitrate Tests.

CHAPTER XXII

SODIUM AND ITS COMPOUNDS

272. Manufacture of sodium. — Sodium is manufactured by the electrolysis of melted sodium hydroxide — a method discovered by the English chemist Davy (Fig. 103). Figure 104 is a sketch of one form of apparatus used at Niagara Falls, where many electrical industries are located.

The body of the steel cylinder (*S*) rests within a heated flue (not shown). The cathode (*C*) is iron and the connected carbon rods (*AA*) constitute the anode. A cylindrical collecting pot *P* surrounds the end of the cathode, and being perforated at the lower end permits the circulation of the fused hydroxide but prevents the escape of the melted sodium in the upper part.

The sodium hydroxide in the neck *B* is solid, but is kept melted and at about 300° C. in the main part by auxiliary gas flames.

The sodium hydroxide conducts an electric current just as a solution does. As the electrolysis proceeds, sodium and hydrogen ions (Na^+ and H^+) migrate to the cathode (*C*). Here they are discharged, thereby producing sodium and hydrogen, which rise, and collect in the cylindrical pot *P*. The hydrogen escapes to some extent from under the cover, but enough always remains in the upper part of *P* to protect the sodium



FIG. 103. — The English chemist Davy (1778–1829), who first prepared sodium by the electrolysis of sodium hydroxide in 1807.

from the air. The molten sodium, which floats on the top of the fused sodium hydroxide, is skimmed off at intervals and poured into molds.

Oxygen ions (O^{--} from the OH ions) migrate to the anode, are discharged, and produce oxygen (gas), which escapes through the pipe O without coming in contact with the sodium or hydrogen.

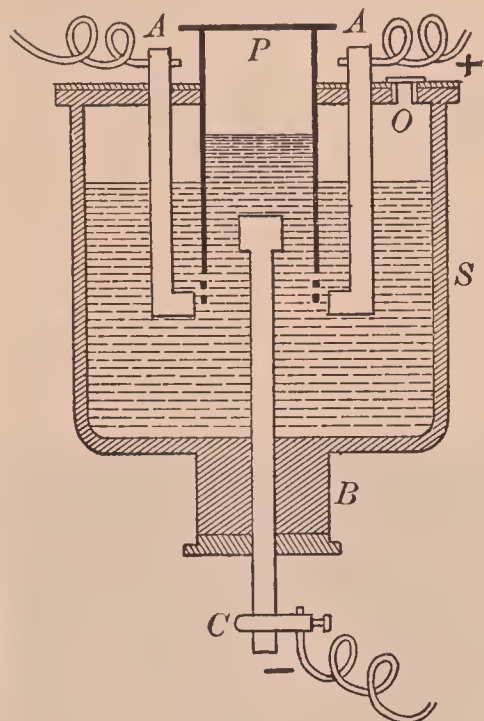


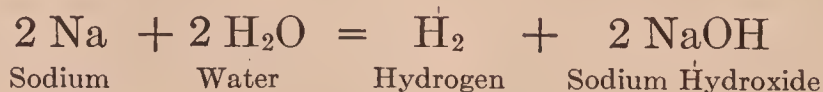
FIG. 104. — Sketch of the apparatus for manufacturing sodium.

273. Physical properties of sodium. — Sodium is a silver-white metal. It is so soft that it can be easily cut with a knife. It floats on water, since its specific gravity is only about 0.97.

274. Chemical properties of sodium. — Heated in air, sodium melts at $96^{\circ}C$. At a higher temperature it volatilizes and burns with a brilliant yellow flame, forming sodium peroxide (Na_2O_2). This intense yellow color is characteristic of sodium and its compounds and is the usual **test for sodium** (free or combined). (Potassium compounds, which are much like the corresponding sodium ones, color the flame a pale violet — thus being readily distinguished from sodium compounds.)

In moist air the bright surface of sodium quickly tarnishes. Hence the metal usually has a yellow or brownish coating (instead of a shiny surface). It is kept under kerosene or a liquid free from water.

Sodium decomposes water at ordinary temperatures, thus: —



If held in one place upon the water by filter paper, enough heat is generated by the reaction to set fire to the hydrogen, which burns with a yellow flame, owing to the presence of volatilized sodium (§ 69). It combines vigorously with many non-metals, especially chlorine. If chlorine is passed through a tube containing melted sodium, the two elements

combine with a brilliant flame, forming sodium chloride. In this way Davy in 1810 proved that common salt is sodium chloride.

275. Sodium chloride. — This is the most important compound of sodium. It is familiar under the name of **salt** or **common salt**. It is one of the most abundant substances and is the chief source of sodium compounds.

276. Preparation of common salt. — Salt is obtained from sea water, rock salt deposits, and brines. The sea water is evaporated, often by exposure to the sun, and the salt separates from the concentrated solution. Deposits of salt are found in many parts of the globe, the most important being in England and Germany. The salt is dug out and then purified by recrystallization from water. In some parts of the United States natural or artificial brines are evaporated in large vacuum pans and then crystallized to the proper size in special apparatus.

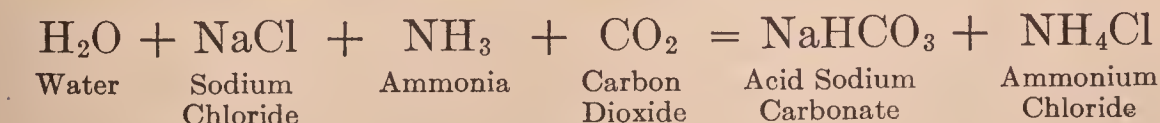
The dampness of salt is due to traces of magnesium and calcium chlorides which absorb moisture from the air (§ 94). Pure salt does not absorb moisture. Sometimes certain harmless substances are added to salt to keep it dry.

277. Properties and uses of sodium chloride. — Sodium chloride is rather uniformly soluble in water, 100 gm. of water dissolving about 36 gm. of salt at 20° C., and about 39 gm. at 100° C. (Fig. 42). It crystallizes in cubes, and does not contain water of hydration (§ 85).

Salt is an essential ingredient of the food of man and animals. Besides its universal domestic use, enormous quantities are used in making sodium carbonate, sodium hydroxide, chlorine (§ 121), and hydrochloric acid (§ 130).

278. Sodium carbonate. — This substance (Na_2CO_3) was formerly obtained from the ashes of marine plants. Now it is manufactured by the Solvay process.

279. The Solvay process. — This consists in saturating a cold concentrated solution of sodium chloride with ammonia and carbon dioxide. The equation is: —



The acid sodium carbonate is sparingly soluble in cold ammonium chloride solution, and hence is precipitated. The

acid sodium carbonate is filtered off and then changed into normal sodium carbonate by heating, thus:—



Acid Sodium
Carbonate

Sodium
Carbonate

Carbon
Dioxide

Water

In operating the Solvay process (Fig. 105), a concentrated solution of sodium chloride is saturated with ammonia (in *D*), warmed to 40°

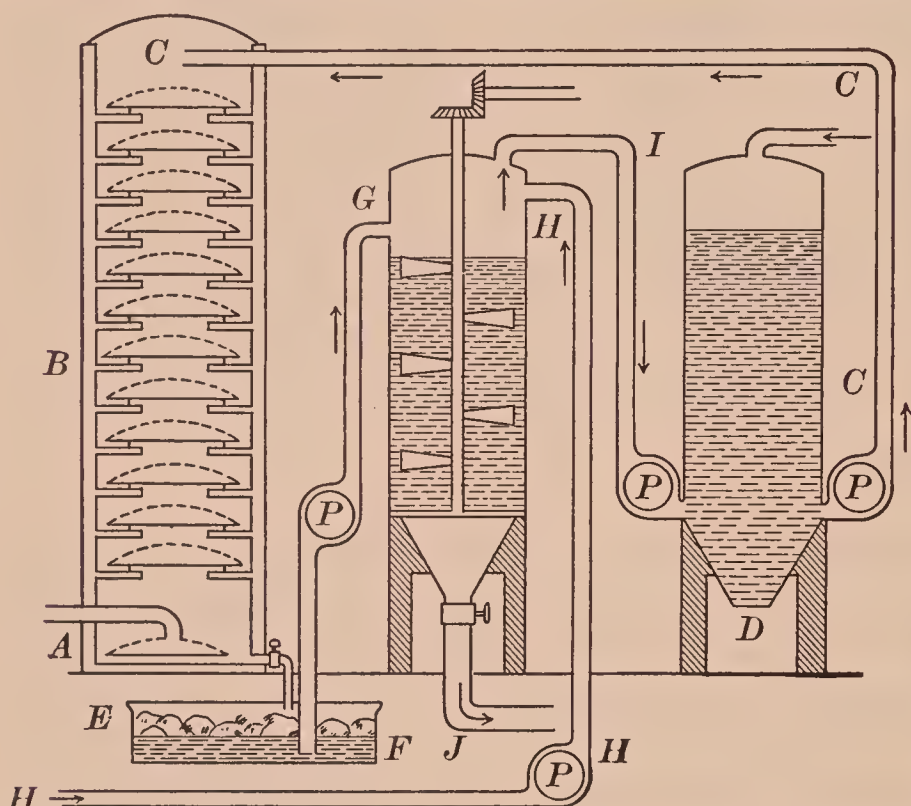


FIG. 105. — Sketch of the apparatus for manufacturing sodium carbonate (and bicarbonate) by the Solvay process. (Pumps marked *P*.)

sodium carbonate and ammonium chloride. Both pass into *E*, *F*. The precipitate of acid sodium carbonate is filtered off and changed by heating into normal sodium carbonate (Na_2CO_3). The ammonium chloride solution is pumped into *G*, where it reacts with calcium hydroxide forced in through *H*; the liberated ammonia passes through *I* into *D*, and the calcium chloride is drawn off through *J*. The carbon dioxide liberated by heating the sodium bicarbonate is used in *B*.

C., and run (by *C*, *C*, *C*) into a tower (*B*) fitted with perforated partitions. Carbon dioxide is forced into the bottom (at *A*), and forms carbonic acid, which reacts with the ammonium hydroxide to produce ammonium bicarbonate,



This salt reacts with the sodium chloride and produces acid

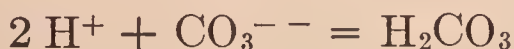
280. Properties and uses of sodium carbonate.—Crystallized sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$), often called **soda crystals**, **sal soda**, or **washing soda**, effloresces, *i.e.*, it slowly loses its water of hydration when exposed to air (§ 86). When heated, it first dissolves in its water of hydration, and

finally changes into the white anhydrous salt (Na_2CO_3) which is called **soda ash** or **calcined soda**.

It is soluble in water, and forms an alkaline solution which is widely used as a cleansing agent; hence the name **washing soda**.

Enormous quantities are consumed in the manufacture of glass, water glass (sodium silicate), soap, borax, sodium hydroxide, and many other useful substances.

281. Hydrolysis of sodium carbonate. — The alkaline reaction of sodium carbonate is due to hydrolysis and can be explained in terms of the ionic theory. Hitherto water has been called a non-electrolyte, *i.e.*, it does not ionize. As a matter of fact it does form the ions H^+ and OH^- , but to such a very slight extent that they have little or no effect in most cases. Under certain conditions, however, these ions (H^+ and OH^-) participate in reactions, *e.g.*, with sodium carbonate. Sodium carbonate ionizes into 2Na^+ and CO_3^{--} , but the unstable CO_3 -ions form HCO_3 -ions with the H-ions from the slightly dissociated water. This removal of H-ions finally leaves in the solution sufficient OH -ions to produce an alkaline reaction. Equations for these ionic reactions are: —



We may define **hydrolysis** as a chemical change in which water is an essential factor. A more restricted definition is the interaction of the ions of water with the ions of certain salts. A salt derived from a weak acid (*e.g.*, H_2CO_3) and a strong base (*e.g.*, NaOH) gives an alkaline solution. On the other hand, a salt derived from a strong acid (*e.g.*, H_2SO_4) and a weak base (*e.g.*, $\text{Cu}(\text{OH})_2$) gives an acid solution. Thus, copper sulfate solution has an acid reaction.

282. Sodium bicarbonate. — This substance is prepared by the Solvay process (see above), or by treating sodium carbonate solution with carbon dioxide.

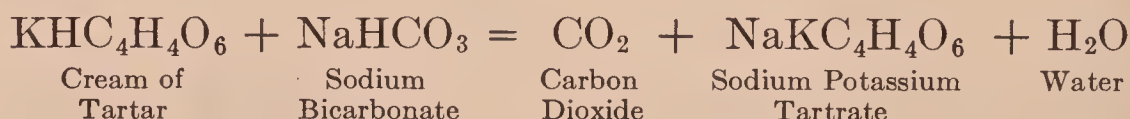
Sodium bicarbonate is a white powder, less soluble in water than the normal sodium carbonate. When heated alone or

when mixed with an acid or an acid salt, sodium bicarbonate liberates carbon dioxide. This property early led to its use in cooking, and gave the names **cooking soda**, **baking soda**, or simply **soda**.

Sodium bicarbonate is sometimes called **acid sodium carbonate** (though it is nearly neutral to litmus) and also sodium hydrogen carbonate. The neutral reaction of a solution of sodium bicarbonate is due to the fact that neither of its ions (Na^+ and HCO_3^-) affects litmus. It should be noted that the name "acid" sodium carbonate emphasizes the method of formation (from carbonic acid), not the properties of the salt (§ 169).

283. Baking powders. — Sodium bicarbonate is an essential ingredient of baking powders and of the various mixtures (except yeast) used to raise bread, cake, and other food. The other ingredient is a substance which has a weak acid reaction, such as acid calcium, or acid sodium, phosphate ($\text{CaH}_4(\text{PO}_4)_2$ or NaH_2PO_4), cream of tartar (acid potassium tartrate ($\text{KHC}_4\text{H}_4\text{O}_6$)), or alum ($\text{K}_2\text{Al}_2(\text{SO}_4)_4$). Commercial baking powders contain a small proportion of starch or flour, which prevents (or retards) premature chemical action.

If baking powder is mixed with water, carbon dioxide is slowly liberated. With a tartrate baking powder the equation is: —



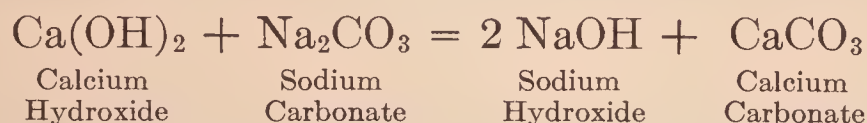
When dough is raised with baking powder, or with a mixture of baking soda and cream of tartar, the escaping carbon dioxide puffs it up. Hence baking soda is often called **saleratus** — the salt that aerates (from the Latin words *sal*, salt and *aer*, air).

284. Sodium hydroxide or caustic soda. — This substance is a white, crystalline, brittle, corrosive solid. It absorbs water (*i.e.*, deliquesces — § 94). It also absorbs carbon dioxide rapidly from the air, and is thereby changed into sodium carbonate. It is very soluble in water, and dissolves with rise of temperature. The solution is strongly

alkaline and disintegrates many organic substances, *e.g.*, wool, but not cotton. Hence the term *caustic*. It is a strong base and its solution contains a high per cent of hydroxyl ions (§ 185). The solution is sometimes called **lye** or **soda lye**.

Large quantities are used in refining petroleum and vegetable oils, and in making soap, paper pulp, phenol (carbolic acid, C_6H_5OH), and chemicals such as chlorates, hypochlorites, and nitrites.

285. Manufacture of sodium hydroxide. — The **chemical process** consists in boiling a dilute solution of sodium carbonate with calcium hydroxide; the main change is represented thus: —



The solution of sodium hydroxide is filtered from the insoluble calcium carbonate and evaporated. The residue is heated, and the molten mass is then poured into small cylindrical molds about the diameter of a lead pencil or into large iron barrels called drums. Some is made into flakes.

In the **electrolytic process**, a solution of sodium chloride is used. When an electric current is passed through such a solution, sodium hydroxide and hydrogen are produced at the cathode and chlorine at the anode. The cells are constructed to prevent secondary action between the sodium hydroxide and chlorine (which would produce sodium hypochlorite or bleach liquor). A view of the cell room in an electrolytic alkali plant is shown in Fig. 106.

Several types of electrolytic apparatus are used. Only one — the porous diaphragm type — will be described here. An example of this type is shown in Fig. 107. The liquid can penetrate the porous diaphragm. Hence the diaphragm does not interfere with the flow of the electric current, but it does prevent the mixing of the two solutions. The porous diaphragm is a sheet of asbestos (mixed with iron oxide), which is supported on the perforated iron cathode. The graphite anode dips into the sodium chloride solution in the middle compartment; here the solution is kept at a certain level by regulation of the inflow. The outer compartment contains kerosene.

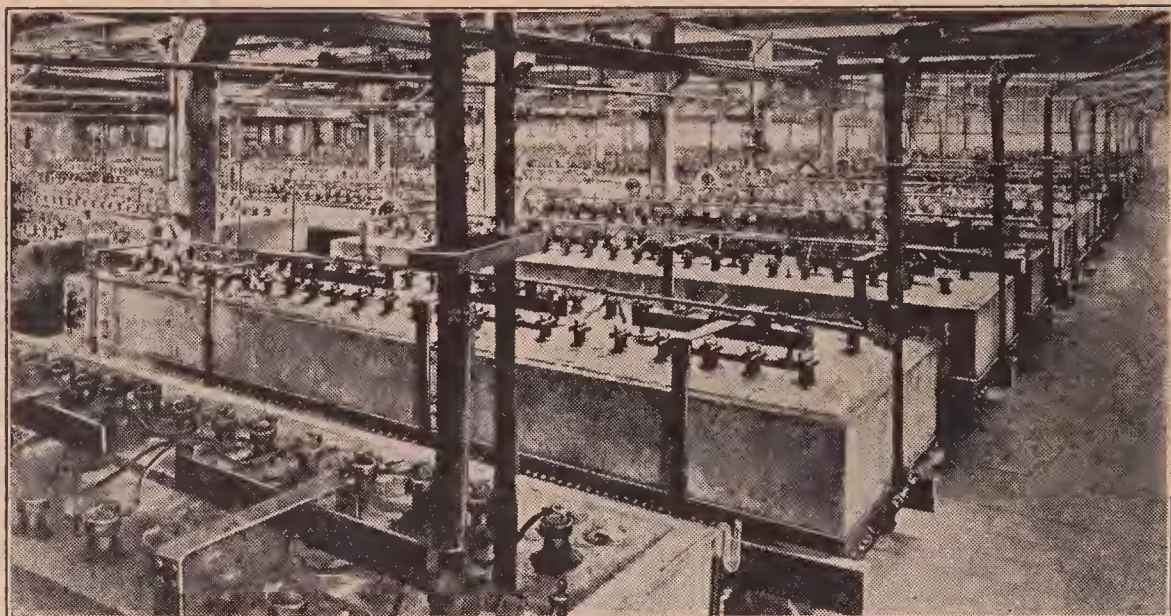


FIG. 106. — The cell room of a plant for making sodium hydroxide by electrolysis.

When the current is passing, the sodium ions (Na^+) migrate to the cathode, lose their charges, and become sodium atoms (Na). The sodium atoms interact with the water and form sodium hydroxide and hydrogen. The sodium hydroxide drops through the kerosene

to the bottom of the outer compartment, and is drawn off through *C*; the hydrogen escapes through *B*. Similarly, chlorine ions (Cl^-) migrate to the anode, lose their charges, and become chlorine atoms (Cl) which unite and escape as chlorine gas (Cl_2) through *A*. The equations may be written thus: (1) $\text{NaCl} = \text{Na}^+ + \text{Cl}^-$; (2) $2 \text{Na}^+ = 2 \text{Na}$ and $2 \text{Cl}^- = \text{Cl}_2$; (3) $2 \text{Na} + 2 \text{H}_2\text{O} = 2 \text{NaOH} + \text{H}_2$.

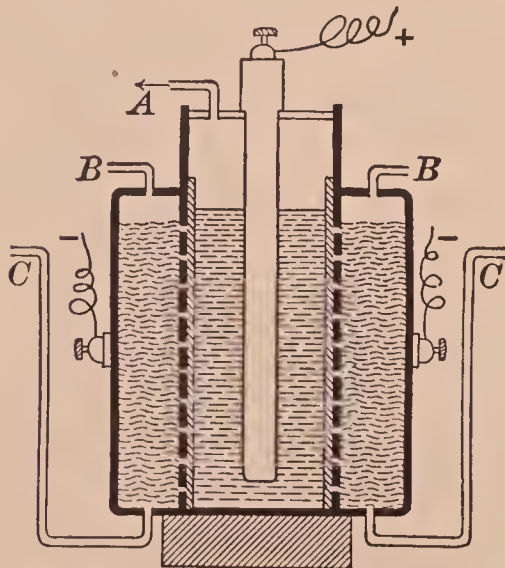


FIG. 107. — Sketch of the diaphragm type of apparatus for the manufacture of sodium hydroxide by the electrolysis of sodium chloride solution.

The sodium hydroxide solution is treated (without filtering) as described above (second paragraph, this section). The chlorine is stored or compressed into metal cylinders or is made directly into bleaching mixtures.

286. Sodium tetraborate or borax. — This substance is a white crystalline solid, having five or ten molecules of water of hydration. A common household form of borax is the

powdered crystals. The crystals readily effloresce and crumble in the air (§ 186.) When heated, crystallized borax loses its water of hydration and swells into a white porous mass, which finally melts into a glass-like solid. This glassy borax dissolves metallic oxides and is colored by them.

When borax is melted on the end of a looped wire, the transparent globule is called a **borax bead**. These beads assume different colors if the bead is touched with a minute fragment of a metallic compound and then heated in an oxidizing or a reducing flame (Fig. 108). The colors are characteristic of the metals. Thus, a copper bead is made blue-green by an oxidizing flame and red by a reducing flame.

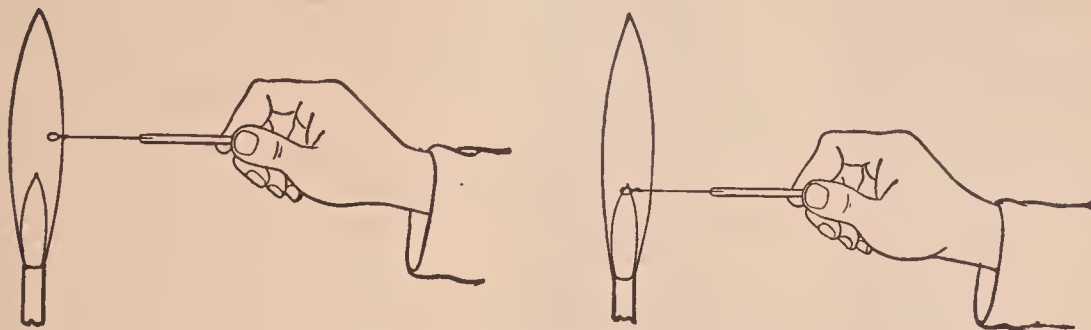


FIG. 108. — Testing for a metal with a borax bead in the oxidizing flame (left) and reducing flame (right).

Borax beads are used in testing for metals, *e.g.*, often in a small quantity of a mineral.

Its power to react with oxides adapts borax for use in soldering and welding metals. Solder adheres only to clean metals, so a little borax is used to dissolve the film of oxide on the surfaces to be joined.

Borax is chiefly used in the manufacture of enamels for coating iron ware. The so-called “granite” or “agate” ware and “porcelain-lined” vessels are made of iron coated with an easily fused borax glass called enamel. Considerable borax is used for preserving meat, fish, cheese, and other foods, because it prevents the growth of certain bacteria.

A solution of borax has a slight alkaline reaction owing to hydrolysis (§ 281); hence it is sometimes used instead of soap as a cleansing agent. Some soaps contain borax.

287. Sodium nitrate. — This substance is found abundantly only in Chile and is often called **Chile saltpeter**. It

is extracted by dissolving out the saltpeter from the earthy matter and crystallizing the solution. The liquid left from



FIG. 109. — Result of an experiment with potassium salts. The pot on the left received a complete fertilizer, while the pot on the right differed only in receiving a fertilizer *without* potassium salts.

the crystallization is a source of iodine (§§ 435, 436). It is a white or brownish solid, which becomes moist in the air, owing to slight deliquescence (§ 94). Large quantities are used as a fertilizer, either alone or mixed with compounds of potassium and of phosphorus (§ 143). It is used in making nitric acid (§ 197) and potassium nitrate.

288. Fertilizers containing potassium. — Potassium, like nitrogen and phosphorus, is essential to the life of plants and animals. Potassium salts are taken from the soil by plants and must be returned if the soil is to

be productive. Sometimes wood ashes are applied to the soil. Usually the potassium salts, *e.g.*, potassium chloride, are supplied in the form of fertilizer. Experiments show that many soils need potassium salts as plant food (Fig. 109). (Compare §§ 143, 300.)

EXERCISES

1. Describe the manufacture of sodium.
2. Summarize (a) the physical properties and (b) the chemical properties of sodium.
3. Give an outline of the manufacture of sodium carbonate. Write the essential equations.
4. What is (a) soda, (b) soda ash, (c) sodium carbonate, (d) soda

crystals, (e) sal soda, (f) washing soda, (g) calcined soda, (h) acid sodium carbonate, (i) saleratus, (j) baking soda, (k) caustic soda?

5. Describe the manufacture of sodium hydroxide by (a) the chemical process and (b) the electrolytic process.

6. What is the flame test for (a) sodium, (b) sodium compounds, (c) potassium compounds?

7. Why does sodium carbonate form an alkaline solution?

8. Give the name and formula of the ions in dilute solutions of (a) sodium hydroxide, (b) sodium chloride, and (c) sodium nitrate.

PROBLEMS

1. Calculate the weight of sodium in (a) 20 gm. of NaOH, and (b) 20 gm. of sodium bicarbonate.

2. How many kg. of sodium hydroxide can be made from 1000 kg. of Na_2CO_3 ?

3. What volume of hydrogen is liberated by the reaction of 1 gm. of sodium on water?

4. What is the per cent of sodium in Na_2SO_4 ?

5. Calculate the simplest formula corresponding to Na = 32.39 per cent, S = 22.54, O = 45.07.

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

Exercise S51 — Sodium Bicarbonate — T.

Exercise S52 — Sodium Chloride — T.

Exercise *11 — Reaction between Sodium and Water — T.

Exercise S15B — Deliquescence — T.

CHAPTER XXIII

CALCIUM CARBONATE — OXIDE — HYDROXIDE — SULFATE — PHOSPHATE

289. **Calcium carbonate.** — An abundant form is **limestone**; large deposits are found in many places. Limestone is a white or gray compact solid, but impurities, especially organic matter and iron compounds, produce many colored

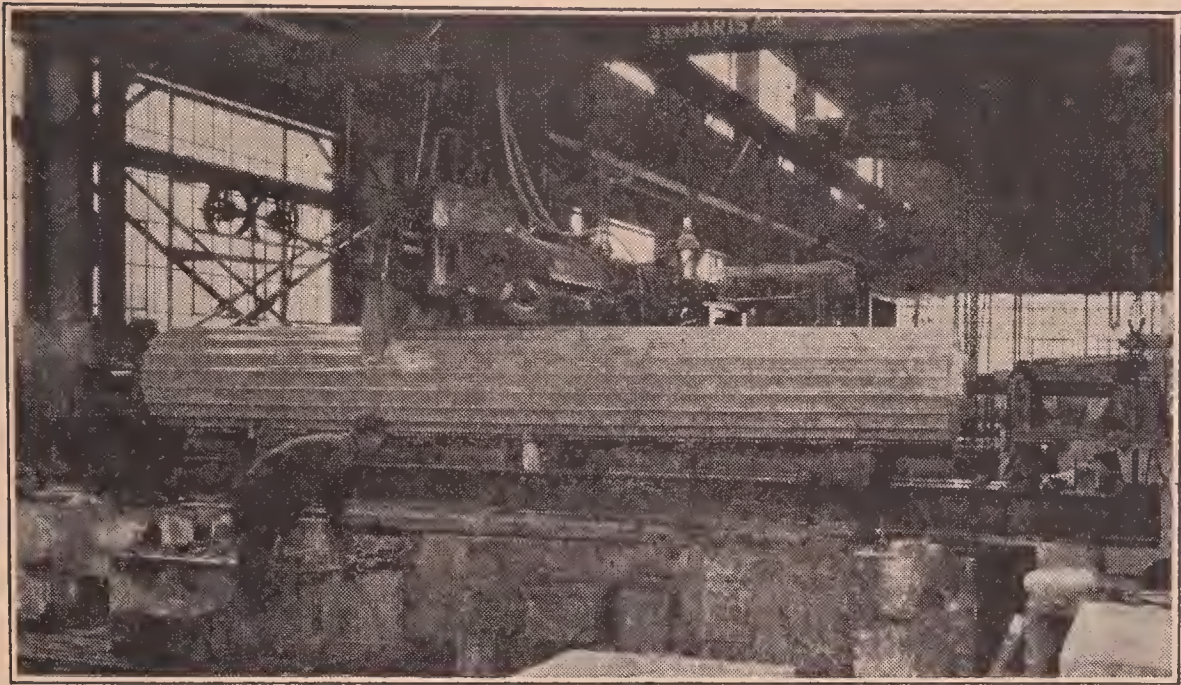


Courtesy Thomsen-Ellis Co.

FIG. 110. — A marble quarry in Georgia.

varieties. Much limestone contains sand and clay. Some varieties contain the fossil remains of plants and animals. Hard, compact, crystalline limestone is called **marble**; it is extensively used as a building and an ornamental stone (Figs. 110, 111, 112). **Calcite** is the purest form of crystallized calcium carbonate.

Enormous quantities of the different varieties of calcium



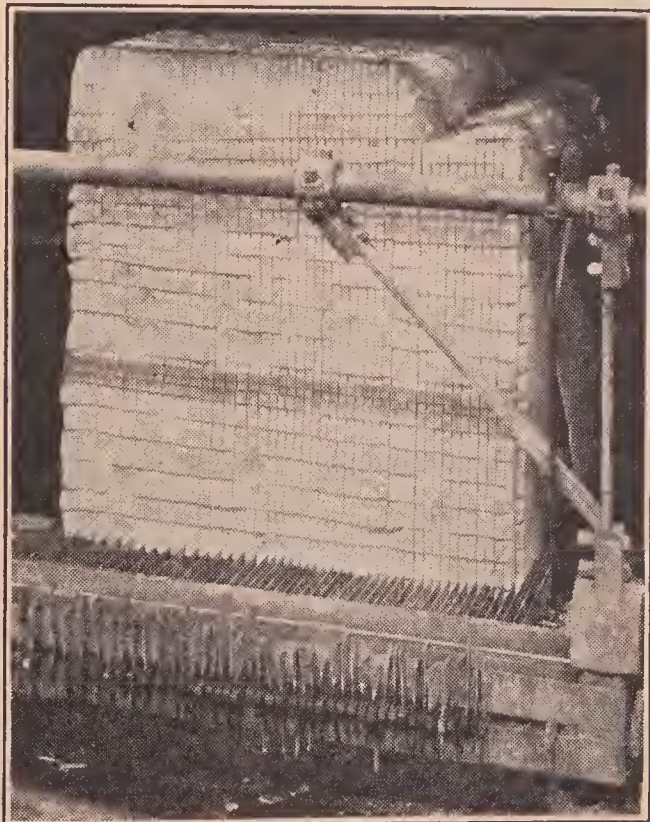
Courtesy Thomsen-Ellis Co.

FIG. 111. — Cutting the flutes in a marble column.

carbonate are used in making lime, cement, glass (§ 449), and sodium carbonate (§ 279), and as a flux in the smelting of metals, *e.g.*, iron (§ 350).

290. Deposition of calcium carbonate. — Calcium carbonate is only very slightly soluble in water. But if the water contains carbon dioxide, the carbonate dissolves, owing to its transformation into the soluble acid calcium carbonate ($\text{CaH}_2(\text{CO}_3)_2$).

Some underground water contains carbon dioxide, and as this water works its way along in limestone regions, the limestone is dissolved and caves are often formed or enlarged. When the water enters a cave and drips from the top, the water evaporates, or the gas escapes, or both, and calcium carbonate is re-deposited, often forming sta-



Courtesy Thomsen-Ellis Co.

FIG. 112. — Sawing a block of marble into slabs with a gang saw.

lactites and stalagmites. **Stalactites** hang from the roof like icicles, and are often exquisitely shaped. **Stalagmites** grow up from the floor. Sometimes the two formations meet and produce a column (Fig. 113). **Mexican onyx** is a variety of stalagmite. Vast deposits of this beautiful mineral are found in Mexico and Algeria. It is translucent and delicately colored, and is used as an ornamental stone, especially for

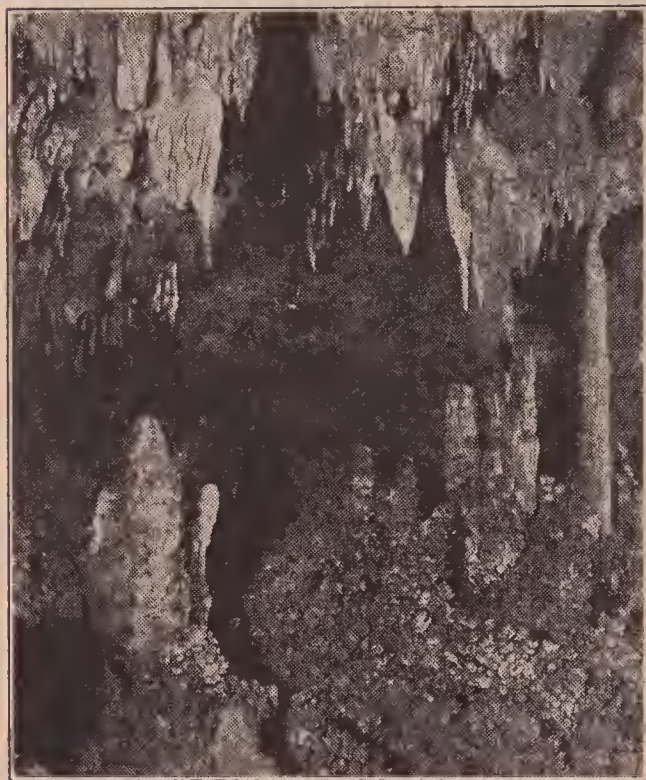


FIG. 113. — Interior of a limestone cave at Luray, Va., showing stalactites and stalagmites.

altars, table tops, mantles, soda fountains, and lamp standards. **Travertine** is another variety; it occurs near many springs in Italy. When fresh it is soft and porous, but it soon hardens and becomes a durable building stone in dry climates. A portion of the walls of the Colosseum and St. Peter's is travertine.

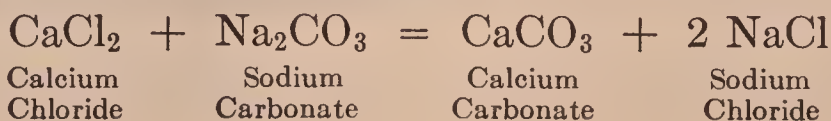
Calcium carbonate which is dissolved in the ocean is extracted by marine organisms and transformed into shells and bony skeletons. The hard parts of these animals accumulate in the mud on the ocean bottom, and subsequently form a part of the land. **Chalk** is the remains of shells of minute marine animals. When examined under a microscope, a good specimen is seen to

consist almost entirely of tiny shells (Fig. 114). **Coral** is calcium carbonate and the vast accumulations in the sea are the skeletons of the coral animals.

291. Chemical properties of calcium carbonate. — Calcium carbonate is decomposed by heat into lime (CaO) and carbon dioxide (§ 293). It interacts with acids (§ 55), *e.g.* :—



Calcium carbonate itself is precipitated by the interaction of a soluble calcium salt and a soluble carbonate, thus :—



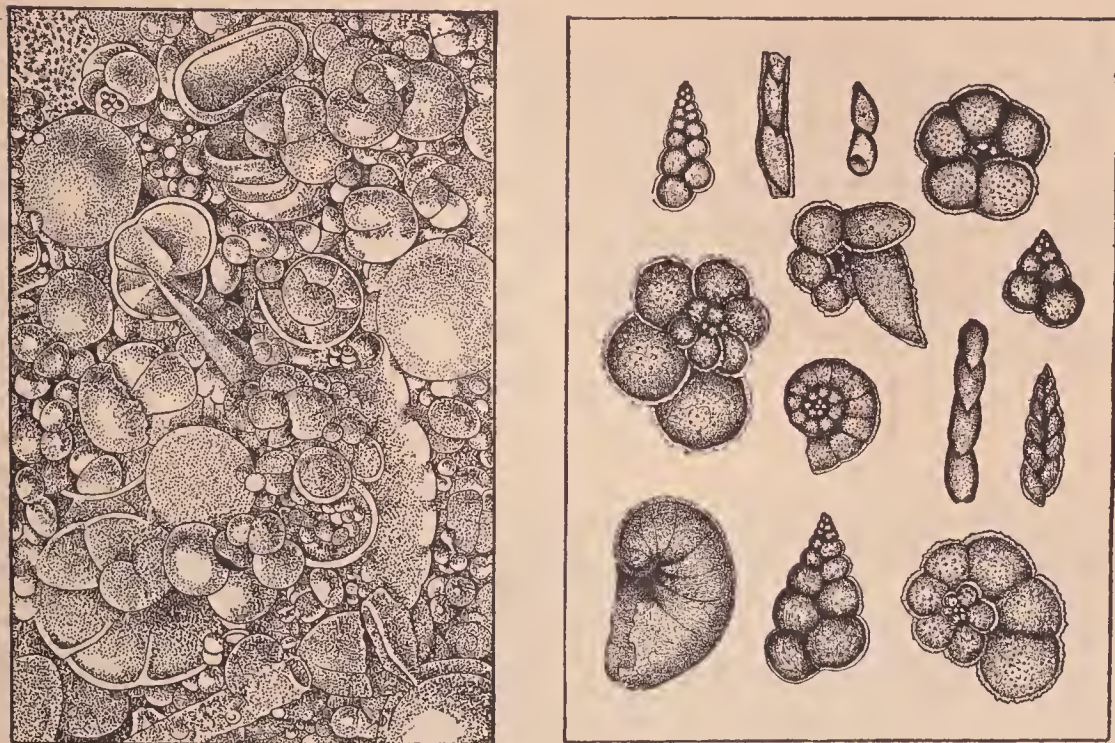


FIG. 114. — Ooze from the ocean bottom showing limestone shells (left), and the same kind of shells (magnified) from chalk deposits in Iowa (right).

This reaction may be used as a **test for a soluble carbonate**, or in preparing a very fine precipitate of calcium carbonate. The **test for an insoluble carbonate** is the liberation of carbon dioxide upon the addition of dilute hydrochloric acid. The liberated gas turns calcium hydroxide turbid. A simple way to make this test is shown in Fig. 115.

Purified calcium carbonate is called **precipitated chalk**, and is used extensively as the polishing ingredient of tooth powder. An impure variety is **whiting**; and a mixture of whiting and linseed oil is **putty**.

292. Lime. — This familiar substance is calcium oxide (CaO). It is a hard, more or less porous, white solid.

Lime when exposed to the air becomes “air slaked,” *i.e.*, it slowly absorbs water and carbon dioxide, swells considerably, and soon crumbles to a

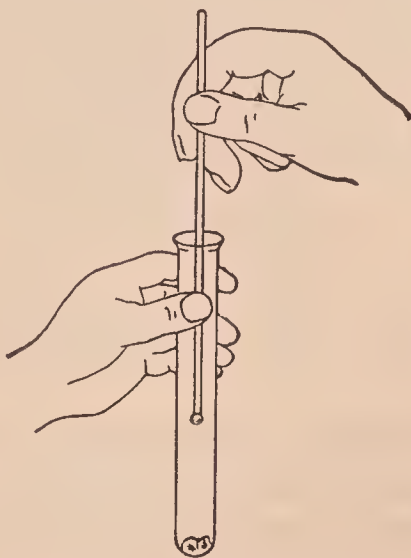


FIG. 115. — Testing for an insoluble carbonate. The carbon dioxide liberated by dilute acid interacts with the drop of calcium hydroxide on the end of the glass tube and forms white, insoluble calcium carbonate.

powder. This powder is a mixture of calcium hydroxide and calcium carbonate; such a mixture is not suitable for many of the uses of lime. (See, however, hydrated lime, § 294.) Lime that is not air slaked is called **quicklime** or **caustic lime**.

When just the right amount of water is slowly added to lime, the two substances combine and form calcium hydroxide or hydrated lime (§ 294). If an excess of water is added

quickly, the lime and water combine vigorously; considerable heat is liberated, as is seen when mortar is being prepared. This operation is called **slaking**, and the product is **slaked lime**. Sometimes water leaks into barrels, cars, or buildings in which lime is stored, and the heat evolved causes a fire.

Large quantities of lime are used in preparing mortar and plaster. Many useful chemicals are made from lime, *e.g.*, bleaching powder (§ 125), calcium carbide (§ 50), sodium hydroxide (§ 285), calcium bisulfite, and lime-sulfur mixtures (§ 204). Considerable lime is used in such industrial operations as purifying illuminating gas, refining sugar, softening

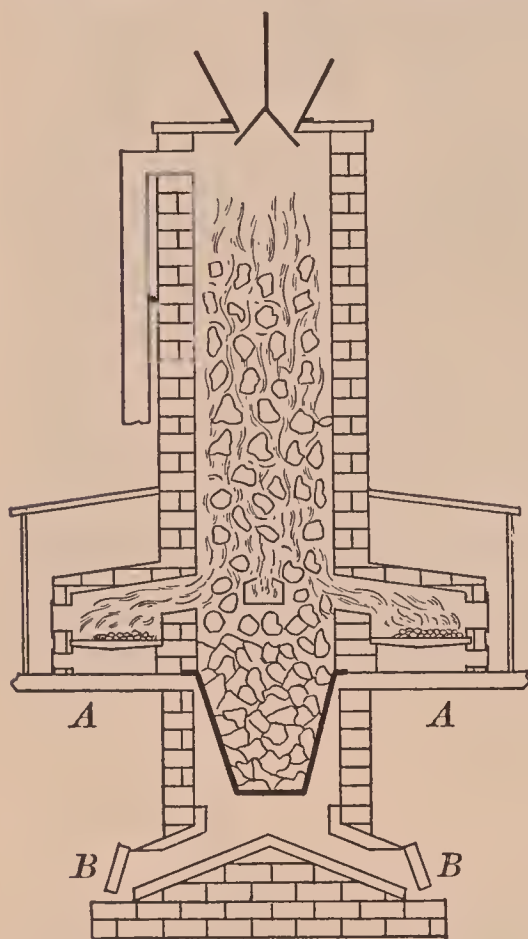
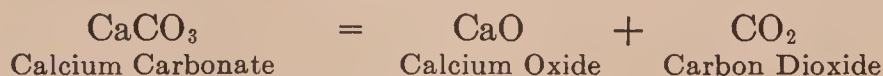


FIG. 116. — Sketch of a continuous vertical limekiln.

water, removing hair from hides, bleaching cotton cloth, and extracting metals from ores. In agriculture lime is added to sour soil to neutralize the acids.

293. Manufacture of lime. — Lime is manufactured by heating limestone. The decomposition takes place according to the equation: —



The carbon dioxide escapes; the lime is left.

Limestone was formerly “burned” in a cavity on a hillside, and in some regions it is so prepared to-day. An arch of limestone is built

across the cavity above the fire pit, and limestone is introduced until the kiln is full. The arch kilns have been largely replaced by continuous kilns, *i.e.*, either rotary or vertical furnaces (Figs. 116, 117, 118).

A sketch of a vertical kiln is shown in Fig. 116. The heat is produced at *A, A*. The hot air and gaseous products of combustion pass up through the lumps of limestone (fed in at the top) and heat it. The rising gases sweep out the carbon dioxide. A proper temperature (about 750°C.) is necessary. The lime drops down through the furnace and is removed (at *B, B*).

Modern vertical kilns are 60 feet or more high (Fig. 118). They operate continuously and produce from 25 to 60 tons a day according

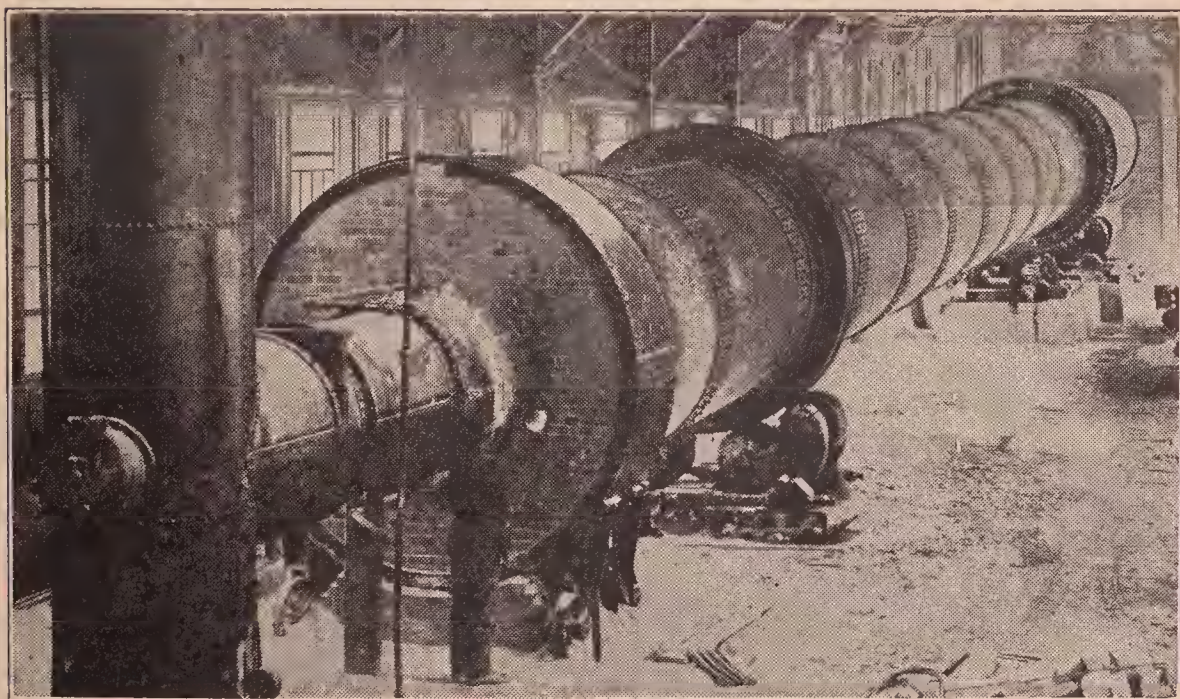


FIG. 117. — A rotary kiln for making lime from marble refuse.

to size. Several towers are often connected with a source of heat, *e.g.*, a gas producer or a furnace burning a smokeless fuel such as coke.

294. Calcium hydroxide.— This substance is a white solid. It is manufactured by adding carefully just enough water to calcium oxide to produce the hydroxide. This **hydrated lime**, as it is called, is a fine white powder. If properly packed, it will keep indefinitely. It can be stored without danger of causing fire, and is suitable for the same purposes as the lime slaked just before use.

Calcium hydroxide is sparingly soluble in water. It is unlike most solids in being more soluble in cold than in warm water. The solution has a bitter taste and a mild alkaline

reaction; it is called **limewater**. Exposed to the air, limewater becomes covered with a thin crust of calcium carbonate, owing to interaction with carbon dioxide. For the same reason, limewater becomes milky or cloudy when carbon dioxide is passed into it. The formation of calcium carbonate in this way is the **test for carbon dioxide**.

Limewater is prepared by carefully adding lime to considerable water, allowing the mixture to stand in a stoppered bottle until the solid has settled, and then removing the clear

liquid with a siphon. When considerable calcium hydroxide is suspended in the liquid, the mixture is called **milk of lime**. Ordinary **white-wash** is thin milk of lime.

295. Mortar.—This is made by mixing lime with three or four times its bulk of sand, and then adding enough water to produce a thick paste. It slowly hardens or sets, owing to the evaporation of water and to the interaction with carbon dioxide.

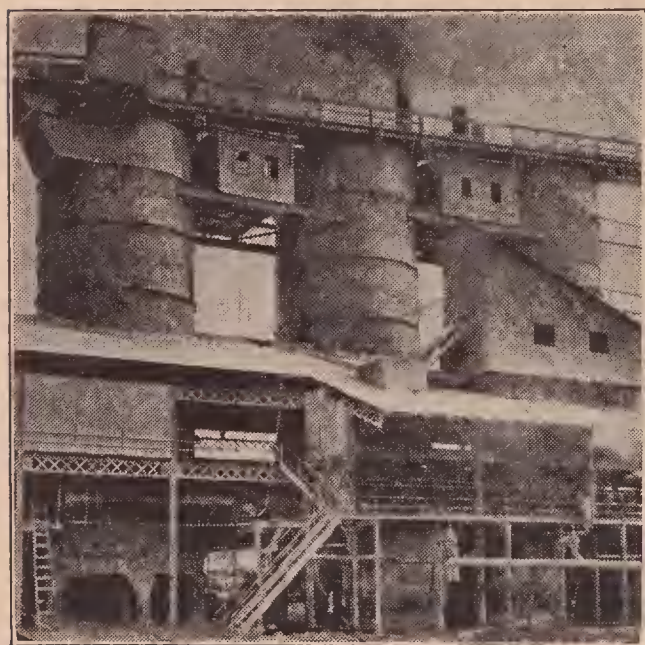


FIG. 118. — A modern vertical limekiln in operation.

When placed between bricks or stones it holds them firmly in place, and is used to construct buildings, walls, foundations, etc.

The sand gives bulk and rigidity; it also makes the mass porous and thus facilitates the change of the hydroxide to the carbonate. We can readily prove that a carbonate is formed by adding hydrochloric acid to a lump of old mortar; the gas which is liberated is carbon dioxide. Hair is sometimes added to make the mortar stick better, especially when it is used as plaster for walls. Hair is not necessary if cement is mixed with the mortar.

296. Cement.—This is a kind of strong, firm mortar. Like ordinary mortar, it hardens in the air; unlike mortar,

however, it hardens under water. The hardening takes place without carbon dioxide.

The chemical changes which occur in the setting of cement are complex and not well understood. The products set into a compact, almost impervious solid.

Cement is next to iron and steel in importance as a building material. Immense quantities (about 100,000,000 barrels, each containing 380 lb.) are made annually in the United States. It is used in a great variety of structures — founda-



FIG. 119. — A huge arch of cement in a railway bridge.

tions, dams, bridges, tunnels, levees, fireproof buildings (*e.g.*, garages), storage tanks, warehouses, grain elevators, floors, walks, and roads (Fig. 119).

A mixture of cement, sand, water, and crushed stone (or coarse gravel) is **concrete**. This mixture is used, usually instead of cement alone, as construction material, particularly for foundations or for walls designed to withstand great pressure, *e.g.*, bridges (Fig. 119). Sometimes **concrete** is **reënforced** by imbedding twisted steel rods or steel sheets in it; the concrete and steel form a firm union, if properly constructed.

Cement is manufactured from a mixture of limestone, clay, and sand. The raw materials must contain the proper proportions of the essential ingredients. The materials are ground very fine, thoroughly mixed, and heated in a steel

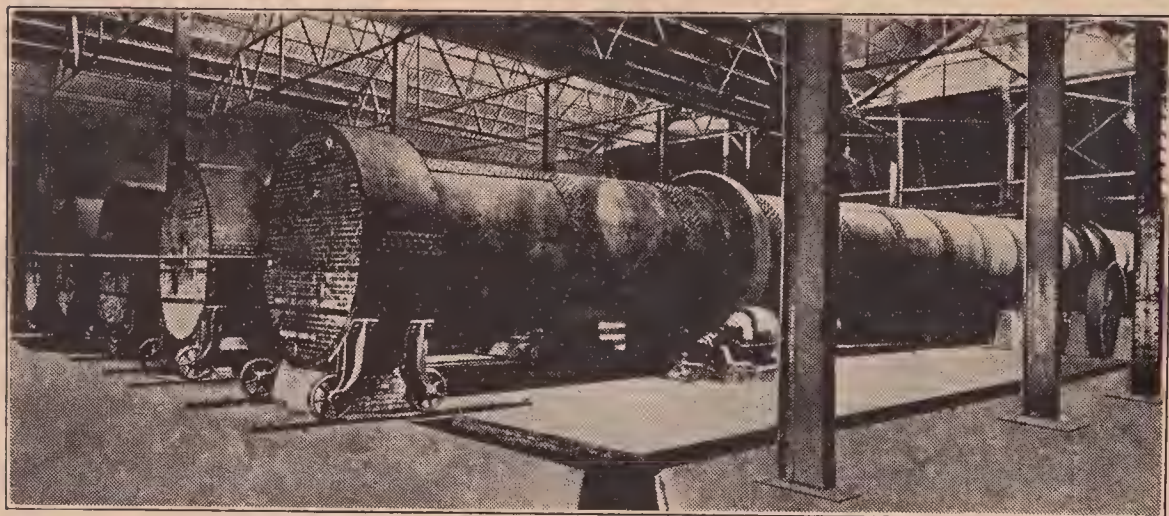


FIG. 120. — Rotary kilns for making cement.

furnace from 70 to 150 feet long and 6 to 8 feet in diameter, and lined with fire-brick. The furnace is inclined about 15 degrees and rotates slowly (about once a minute); it is called a **rotary kiln** (Fig. 120).

The process can be best understood by studying the simple sketch in Fig. 121. The powdered mixture is fed in at the upper end (*C*). As it gradually works its way along through the slowly rotating kiln it is heated to about 1500°C . by the flame and hot gases produced (inside

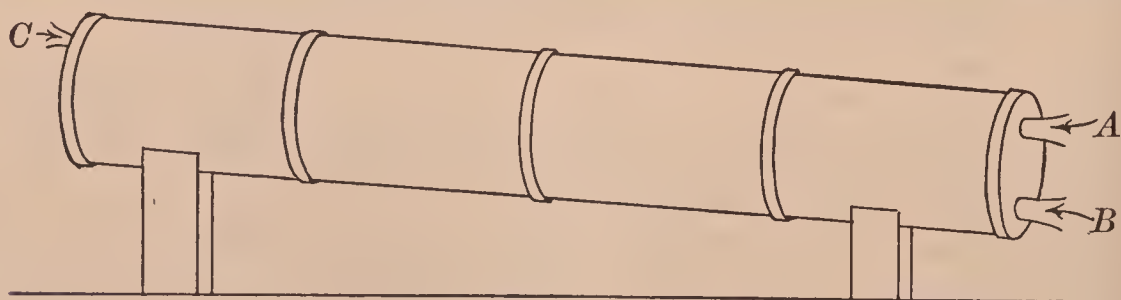


FIG. 121. — Sketch of a cement kiln.

the kiln) by burning oil or coal dust, which is forced in at *A* by a powerful air blast. The mixture forms a semifused, gray-black mass which drops out at *B*. The cooled lumps, called **clinker**, are mixed with about 2 per cent of gypsum (calcium sulfate), and ground to an exceedingly fine powder. This powder, which is grayish, is **cement**.

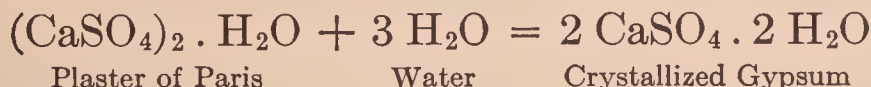
297. Calcium sulfate. — Extensive deposits of different forms of calcium sulfate are found in many localities in the United States. **Gypsum** is the commonest form; it occurs as white masses which have the composition $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$. A translucent, crystallized variety of gypsum is called **selenite**. A variety of crystallized gypsum colored slightly by impurities (*e.g.*, iron compounds) is called **alabaster**. The mineral **anhydrite** is anhydrous calcium sulfate (CaSO_4).

Gypsum is a rather soft solid. It is only slightly soluble in water. It is used as an ingredient of some fertilizers and in making plaster of Paris, paper, white paint, blackboard crayon, cement, and fireproof blocks.

Plaster of Paris is made by heating gypsum to the proper temperature (about 145°C.). The equation is: —



If gypsum is moistened with water, it swells and quickly sets or solidifies to a hard mass which consists of a network of very small crystals. The equation for the setting of plaster of Paris may be written: —



Plaster of Paris

Water

Crystallized Gypsum

Plaster of Paris is used to coat plastered walls, to cement glass to metal, but more largely to make casts and reproductions of statues and small objects. **Stucco** is a mixture of glue and plaster of Paris.

298. Calcium compounds and hardness of water. — Calcium sulfate is slightly soluble in water, and calcium carbonate, as already seen, is changed into soluble acid carbonate ($\text{Ca}(\text{HCO}_3)_2$) by water containing carbon dioxide. Water containing the sulfate and acid carbonate (or the corresponding magnesium salts) is called **hard water**. And water from which they are absent is often called **soft water**.

Soap does not dissolve readily in hard water, but forms, at first, sticky, insoluble compounds with calcium (and magnesium) salts; hence a large quantity of soap must be used.

Hard water, if used in boilers, forms a hard, clinging deposit or “scale” on the inside of the boiler tubes, thus

causing waste of heat (Fig. 122). A deposit one sixteenth of an inch thick causes a loss of about 20 per cent and one fourth inch nearly 50 per cent.

Hardness due to acid calcium carbonate (or acid magnesium carbonate) is called **temporary hardness**, because it can be removed by boiling. Temporary hardness can also be removed by adding the correct amount of calcium oxide or hydroxide to the water to change the soluble to the insoluble carbonate.

Hardness due to calcium sulfate or chloride is called **permanent hardness**, because these salts can not be removed by boiling. (Magnesium sulfate and chloride, like the corresponding calcium salts, produce permanent hardness.) Permanently hard water can be softened by adding the necessary amount of sodium carbonate or sodium phosphate, which converts the calcium and magnesium salts into the insoluble carbonate or phosphate. This process is used on a large scale to soften boiler water. In the home, borax or ammonia may be used.



FIG. 122. — Section of a boiler tube showing the scale deposited by hard water.

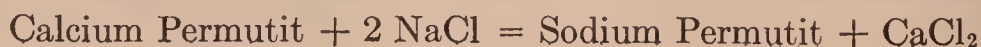
Several industrial processes are used to soften boiler water. One uses a coarse sand-like substance called permutit (essentially an artificial sodium silico-aluminate), which interacts with calcium (and magnesium) compounds, and thereby removes them from the water.

A sketch of the apparatus is shown in Fig. 123. The hard water enters at *A* and slowly filters through the upper layer of marble chips or clean gravel (*B*), the porous layer of the permutit (*C*), the lower layer of gravel (*D*), and out the soft water outlet (*E*). By this process the calcium (and magnesium) replaces the sodium, thus: —

Calcium Sulfate + Sodium Permutit =

Calcium Permutit + Sodium Sulfate

After about twelve hours, the calcium permutit accumulates to such an extent that the mixture no longer reacts. Then water containing sodium chloride is added (from *I*) and allowed to remain long enough (about twelve hours) to regenerate the sodium permutit, thus: —



The permutit is cleaned and the calcium chloride removed by forcing water up through *F* and out at *G*, and the filter is ready for use again.

299. Calcium phosphate.—Calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) is the calcium salt of phosphoric acid (H_3PO_4). It is abundant, being the chief ingredient of bones and phosphate rock. Bones are about 80 per cent calcium phosphate. Phosphate rock is the name given to the hardened remains of land and marine animals. It occurs in large beds in Florida, Tennessee, and North and South Carolina (Fig. 124). Its main constituent is calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$). Artificial phosphate fertilizers are made by treating phosphate rock with sulfuric acid.

300. Relation of phosphorus to life.—Phosphorus is essential to the growth of plants and animals. Plants absorb soluble phosphates from the soil and store up phosphorus compounds, especially in their seeds. Animals eat this vegetable matter, assimilate the phosphorus compounds, and deposit them to some extent in the bones, as well as in brain and nerve tissue. Some of the complex phosphorus compounds in the food consumed by animals are transformed into phosphates. These are eliminated to a large extent, and thus often find their way back into the soil. Here they are taken up again by plants, converted into complex compounds, stored up in the seeds and other parts, which are in turn eaten by animals. And so the process goes on — a phosphorus cycle analogous to the carbon cycle (§ 59, Fig. 24).

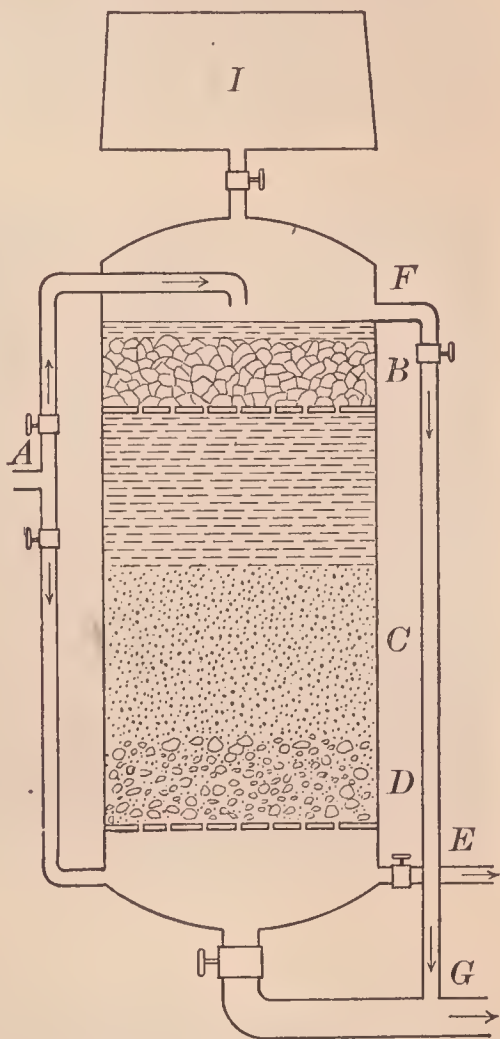


FIG. 123. — Sketch of the apparatus for softening water by the permutit process.

301. Phosphate fertilizers. — In order to furnish plants with phosphorus compounds, various phosphorus-bearing substances are added to the soil in the form of phosphates, especially the fertilizer made from phosphate rock.

The beneficial results of adding (complete) fertilizer to the soil are strikingly shown in Fig. 125. In the wheat field (top), the left was fertilized and the right was unfertilized; the left yielded 17 bushels per acre but the right only 5. The contrast is more conspicuous in the sorghum field (bottom) where the unfertilized part (left) yielded a



FIG. 124. — Mining phosphate rock in Florida. The powerful stream of water washes the phosphate rock down into a pit from which both water and rock are pumped to washers, where sand is removed and low grade rock rejected.

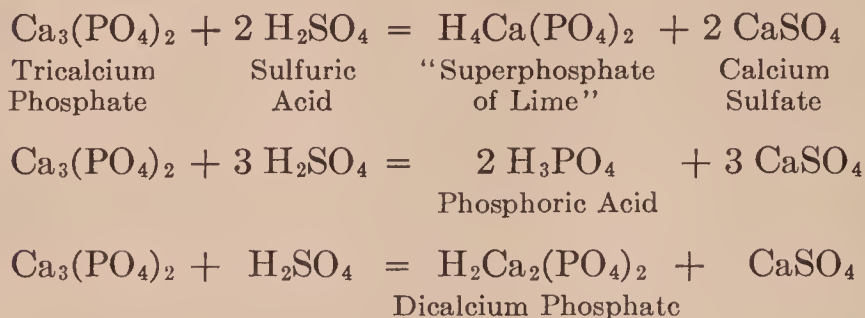
product which gave only 66 gallons of sirup per acre, whereas the right yielded 140 gallons. From the cotton field (middle) about 1350 pounds of seed cotton were obtained from the heavily fertilized part and only about 700 pounds from the scantily fertilized part.

302. Manufacture of phosphate fertilizer. — Tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$), as it is sometimes called, is insoluble in water, and must be changed into the soluble mono-calcium salt ($\text{H}_4\text{Ca}(\text{PO}_4)_2$), so it can be evenly distributed through the soil and easily taken up by plants. This soluble salt is sometimes called “superphosphate of lime.” When



FIG. 125. — Contrast of fertilized and unfertilized fields.

phosphate rock is treated with sulfuric acid, the changes involved may be written thus: —



The mixture of "superphosphate" and calcium sulfate when ground and dried is ready for use as a phosphate fertilizer. Usually "superphosphate" is mixed with compounds of nitrogen (§ 143) and of potassium (§ 288) to form a complete fertilizer.

The law requires the dealer to state the analysis of the fertilizer on the bag or label. The per cent of phosphorus is usually stated as per cent of P_2O_5 , which is popularly called "phosphoric acid."

303. Tests for calcium. — A white solid called calcium oxalate (CaC_2O_4) is formed by the interaction of ammonium oxalate and a dissolved calcium compound; it is insoluble in acetic acid but soluble in hydrochloric acid. Its formation and properties serve as a **test for calcium**. The orange-red color imparted to the Bunsen flame is another test for calcium. (Strontium salts and barium salts, which resemble the corresponding calcium salts, produce a different colored flame — strontium salts crimson and barium salts green.)

EXERCISES

1. State the properties and uses of lime. How is it made?
2. Describe the manufacture of cement.
3. What is hard water? How does it act with soap? What is (a) temporary hardness and (b) permanent hardness? How can each be removed? What is soft water? Why is rain water often called soft water?
4. Write equations for the reactions necessary to prepare (a) calcium nitrate from calcium carbonate, (b) calcium hydroxide from calcium chloride, (c) calcium carbonate from calcium hydroxide.
5. State the tests for calcium.
6. Express the following reactions by equations: (a) calcium hydroxide and carbon dioxide form — and water; (b) calcium carbonate forms — and carbon dioxide.

PROBLEMS

1. Calculate the simplest formula from the following per cents:
Ca = 29.49, O = 46.92, S = 23.59.
2. How many tons of lime can be made from 2000 tons of limestone (95 per cent pure)?
3. How many tons of water are needed to change 1500 tons of lime into calcium hydroxide?
4. What per cent of calcium carbonate is calcium?

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

Exercise *57 — Calcium Carbonate, Oxide, and Hydroxide.

Exercise *58 — Hardness of Water — T.

Exercise S53 — Tests for Calcium in Compounds.

Exercise S54 — Properties of Cement — T.

Exercise S55 — Plaster of Paris — T.

CHAPTER XXIV

IRON AND STEEL — IRON COMPOUNDS

304. Occurrence of iron. — Iron ranks fourth in abundance among the elements and second among the metals (§ 325).

Combined iron is found in most rocks, soils, and natural waters. It is assimilated by plants and animals and is essential to their life processes, being a constituent of chlorophyll (the green coloring matter of plants) and of hæmoglobin (the red coloring matter of blood).

The important ores of iron are hematite (ferric oxide, Fe_2O_3), limonite (hydrated ferric oxide, $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), magnetite (magnetic oxide, Fe_3O_4 or $\text{Fe}(\text{FeO}_2)_2$), and siderite (ferrous carbonate, FeCO_3). The most abundant ore and the chief source of iron and steel in the United States is hematite, which comes mainly from mines in the Lake Superior region.

305. How iron is obtained from its ores. — Iron is obtained by reducing its oxides. The ore is mixed with a flux (usually limestone) and carbon (usually in the form of coke) and heated in a blast furnace. The carbon together

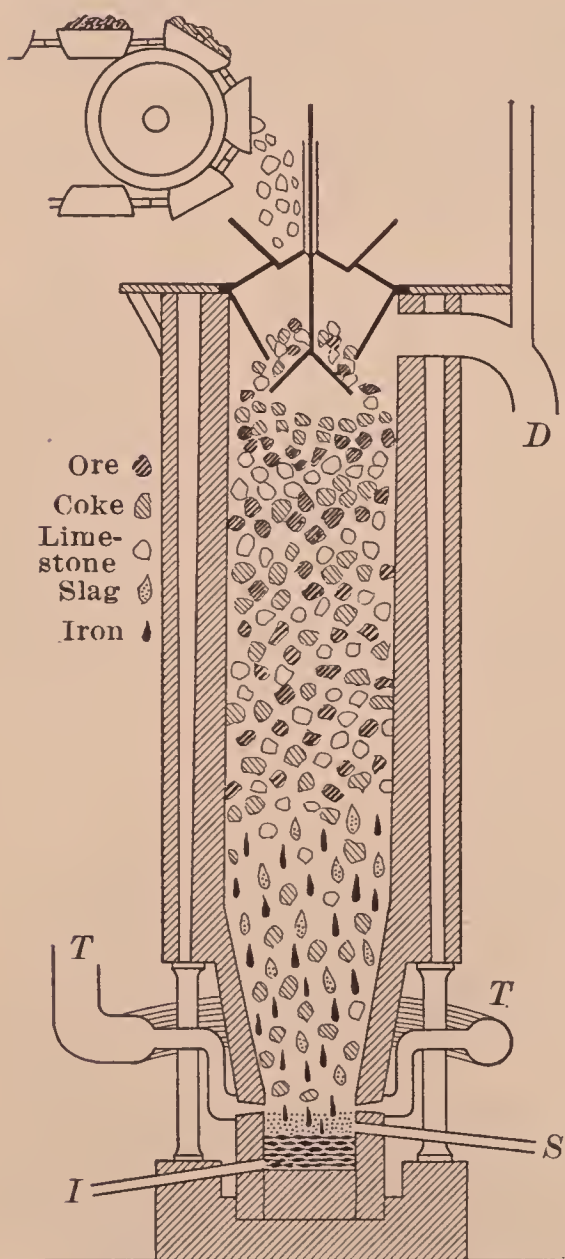


FIG. 126. — Sketch of a blast furnace and the process of smelting iron ore.

with carbon monoxide reduces the oxide to metallic iron. The flux converts the mineral impurities in the ore, called **gangue** (*e.g.*, silicon and aluminum compounds), into fusible silicates called **slag**. The operation, which is called smelting, is carried out in a blast furnace (Figs. 126, 128).

The **blast furnace** (Fig. 126) is a tower, about one hundred feet high and twenty feet in (inside) diameter at the largest part; it is narrower at the top and bottom than in the middle. It is built of steel and lined with fire brick, the walls being several feet thick. Near the bottom is a large pipe encircling the furnace and provided with outlet pipes, called tuyères (*T*), through which large quantities of hot, dry air are forced (*i.e.*, blasted) into the furnace. The air blast is preheated by being passed through chimney-like towers called stoves (Fig. 127) which are between the pair of furnaces (Fig. 128).

Another pipe, *D*, from six to ten feet in diameter (called the "downcomer") permits the escape at the top of the large quantity of hot gases (50 per cent nitrogen and about 25 per cent each of carbon monoxide and dioxide). Gases from the "downcomer" *D* (Fig. 127) enter the stove at the bottom and meet air at *A*. The burning gases pass up and down, heat the checkerwork (shown in cutaway part at left), and escape into the chimney at *C*. To operate, dry air is blown in at *B* which passes up and down the hot checkerwork, and out through *E* to the tuyères *T*.

When the blast furnace is in operation, charges of the proper proportions of ore, coke, and flux are hauled up an inclined track on the furnace in small cars, and introduced at intervals by dumping them upon the cone-shaped cover. The latter is constructed and operated so that the charge is

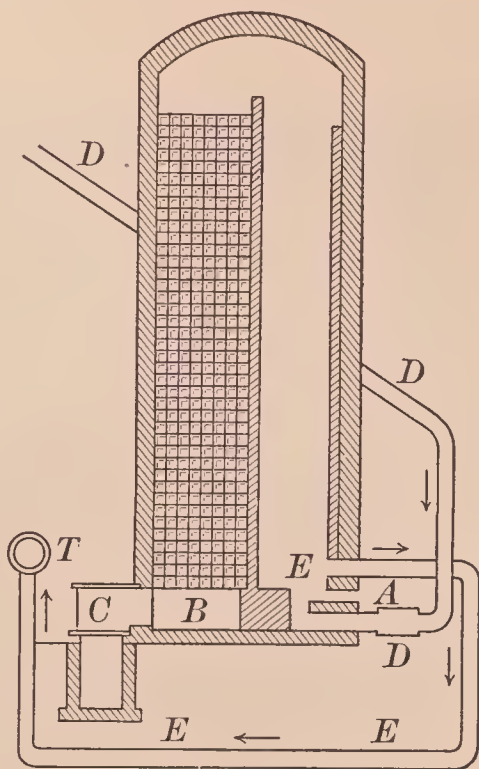


FIG. 127. — Section of a blast furnace stove.

distributed uniformly in layers of ore, coke, and limestone without letting out gases or interrupting the smelting. The hot, dry air which enters at the bottom, through the tuyères (*T*), changes most of the carbon (coke) in the lower part of the furnace into carbon dioxide and thereby generates intense heat. The carbon dioxide is largely reduced by the hot carbon (coke) above it to carbon monoxide, which rises through the furnace and reduces the iron oxide to iron. As the mixture of ore, coke, and limestone settles down through

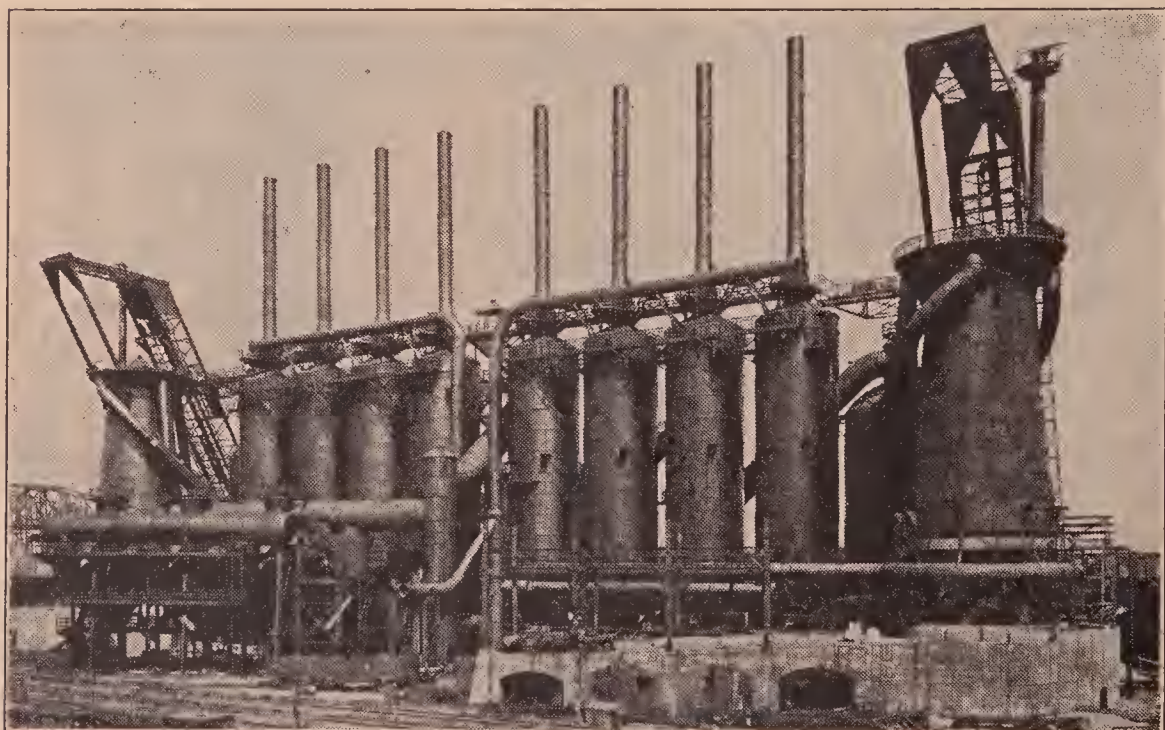


FIG. 128. — Blast furnaces (at ends) and stoves (in the middle).

the furnace, smelting proceeds continuously, *i.e.*, the ore is reduced to metal and the flux forms a slag (largely calcium silicate, CaSiO_3). Both iron and slag sink, the molten iron finally falling through the slag to the bottom of the furnace, where they form two layers.

The molten slag, which floats on the molten iron, is tapped off (at *S*), granulated by running it into water, and carted to the “dump.” It is used to some extent as ballast or dust-preventer for railroads, and to make mineral wool, paving stones, and cement.

The iron is tapped off (at *I*) into huge ladles, run from the furnace into molds of sand or iron (*i.e.*, in a casting machine),

and allowed to solidify into blocks (called “pigs”) weighing 75 to 100 pounds. Such iron is called **cast iron** or **pig iron**. In some plants the molten iron is run into a casting machine (Fig. 129), or into huge vessels, called converters, and made into steel (§ 310).

306. Cast iron. — The cast iron or pig iron that comes from a blast furnace is impure iron. It contains from 92 to 94 per cent of iron, 2.5 to 4.5 of carbon, 1 to 3 of silicon, about

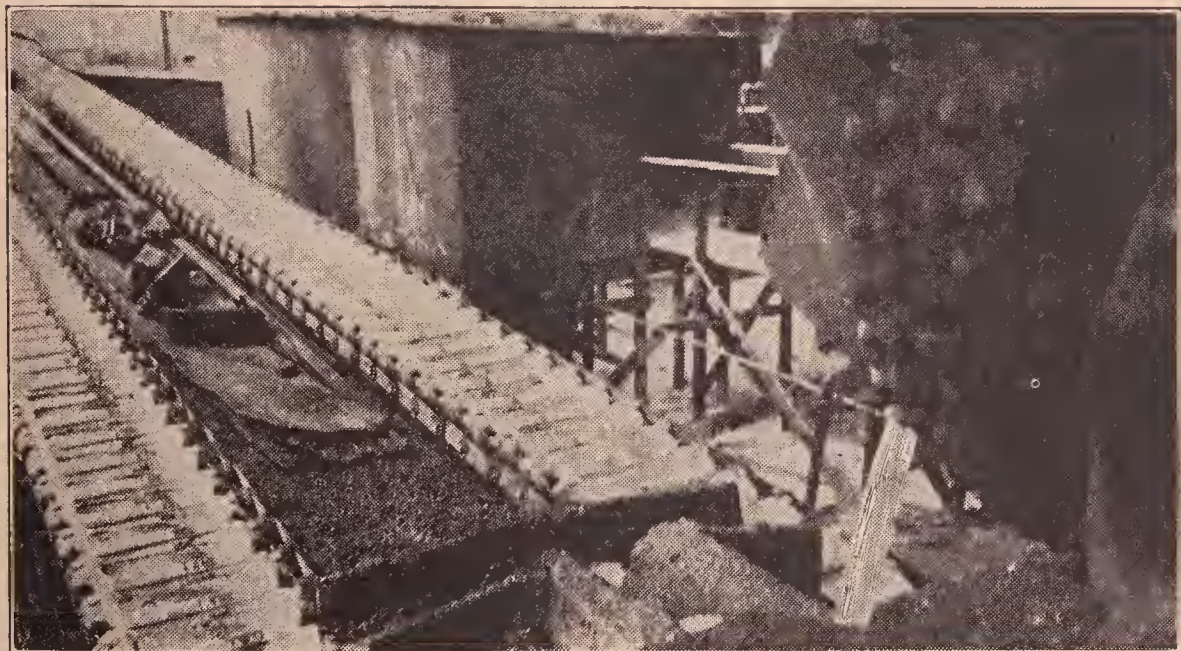


FIG. 129. — Cast iron flowing from a ladle into one end of a long casting machine.

0.7 each of manganese and phosphorus, and 0.02 to 0.05 of sulfur.

The properties of cast iron depend on the rate at which the molten iron cools, as well as on the proportions of the ingredients other than iron. If the cooling takes place rapidly (as in the casting machine, Fig. 129), most of the carbon combines with the iron and forms a carbide (Fe_3C), called **cementite**. This variety of cast iron is called **white cast iron**. But if the cooling occurs slowly (as in sand molds), much of the carbon remains uncombined as scales of graphite (called graphitic carbon). This variety of cast iron is known as **gray cast iron**. It is softer and less brittle than the white variety. It also melts at a lower temperature, forms a thinner liquid, and makes better castings.

Cast iron has a crystalline structure and is brittle; but it will withstand great pressure. It can not be welded nor forged, that is, hot pieces can not be united nor be shaped by hammering. But it can be cast, *i.e.*, melted and formed into a desired shape by pouring the molten metal into a mold.

Cast iron is the variety used in an ordinary iron foundry. Here the iron, which melts at about 1200°C. , is heated in a furnace similar to a blast furnace, and when molten is poured into sand molds of the desired shape. Stoves, pipes, pillars, railings, radiators, parts of machines, and many other useful objects are made of cast iron. Considerable cast iron is made into steel (§ 309).

Cast iron to which 5 to 20 per cent of manganese has been added is called **spiegel iron**, while **ferro-manganese** contains 20 or more per cent of manganese; both are used in making steel.

Cast iron is not attacked by alkalis and only slightly by concentrated acids. Concentrated sulfuric acid is transported in iron tank cars. Cast iron interacts readily, however, with dilute acids.

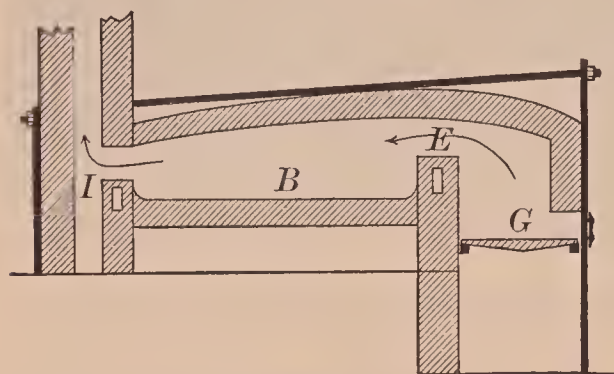


FIG. 130. — Reverberatory furnace.

307. Wrought iron. —

Wrought iron is made from cast iron by removing most of the impurities (carbon, silicon, phosphorus, and sulfur). This can be done by heating the cast iron with iron oxide.

The process is conducted in a reverberatory furnace (Fig. 130). The hearth *B* of the furnace is covered with iron ore (ferric oxide, Fe_2O_3) and the charge of cast iron and flux is laid upon it. The long flame and hot gases from the fire on the grate *G* pass over the bridge *E*, are reflected down upon the charge by the sloping roof of the furnace, and melt the cast iron. Gases escape through *I*. The charge, which rests on *B*, does not come in contact with the fuel on *G*. The carbon in the cast iron unites with the oxygen of the iron oxide and escapes as carbon monoxide. The silicon and

phosphorus are oxidized and react with the flux to form a slag; the manganese and sulfur (in the form of ferrous sulfide) also become a part of the slag. The mixture is stirred or “puddled” with long rods, and as the impurities are removed, the mass becomes pasty.

Finally, large balls, called **blooms**, are removed and hammered, or, more often, rolled between ponderous rollers. This operation squeezes out most of the slag. If the rolling is repeated, the quality of the iron is improved; the final rolling often leaves the iron in the desired commercial shape.

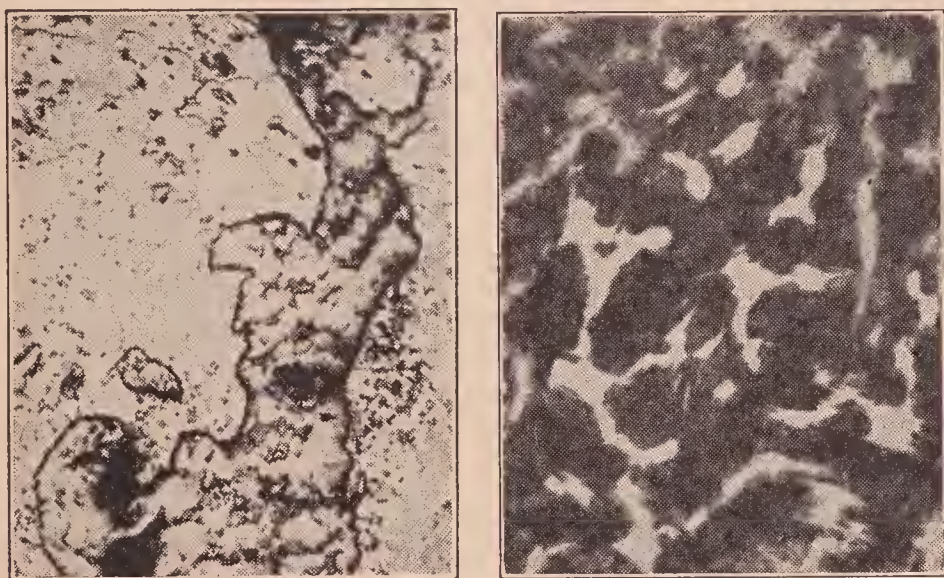


FIG. 131. — Photomicrographs of wrought iron (left) and cast iron (right). The slag can be seen in the wrought iron.

Wrought iron is the purest variety of commercial iron. It is practically pure iron, containing only 2 per cent (or less) of slag (Fig. 131). Wrought iron seldom contains more than 0.5 per cent of carbon and sometimes only 0.06 per cent, the average being about 0.15 per cent; the other elements are present in mere traces.

If a specimen of iron is polished and then etched with weak acid, the microscope reveals the crystalline or other formation and the presence of carbon, slag, carbides, etc. Photographs of a treated specimen of wrought iron and cast iron as seen under the microscope are shown in Fig. 131.

Wrought iron, unlike cast iron, is fibrous and can be bent. Since it softens at about 1000°C. , it can be forged and welded. It is very malleable and ductile, can be readily rolled into

plates and sheets, and drawn into fine wire; in these forms the metal is very strong.

Wrought iron rusts more rapidly than cast iron, and is also more vigorously attacked by acids and alkalis at a high temperature. It is not hardened by sudden cooling (§ 314).

Wrought iron is made into wire, sheets, rods, nails, spikes, bolts, chains, anchors, and agricultural implements. It is less important than formerly, since it is being replaced by soft (*i.e.*, low-carbon) steel (§ 314).

308. What is steel? — We have just seen that cast iron is hard and brittle, whereas wrought iron is soft and tough. Also, that cast iron can be easily melted and poured into

molds, whereas wrought iron softens readily and can be welded. Moreover, cast iron contains a relatively high per cent of carbon (3 to 5), but wrought iron a low per cent (0.15). Between these extremes of composition come the different grades of steel.

The physical properties of the different grades of steel depend not only on the proportions of carbon, phosphorus, silicon, sulfur, etc., but also to a large extent on the method of manufacture and treatment.

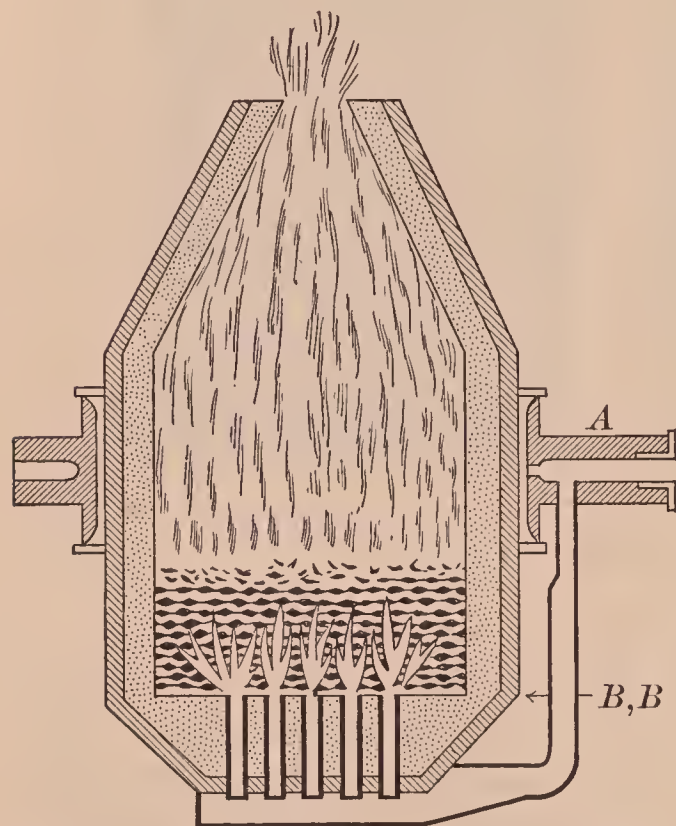


FIG. 132. — Sketch of a converter for making steel from cast iron by the Bessemer process.

309. Manufacture of steel. — Steel is made from cast iron. The aim in the manufacture is to prepare a product containing the desired proportion of carbon but little or no sulfur, phosphorus, and silicon. The steel must also possess specific and known properties. This twofold aim is accomplished by several processes, often supplemented by special treatment.

310. The Bessemer process. — This process consists in (1) burning out most of the impurities in cast iron by an air blast, and then (2) adding carbon and manganese to produce steel of the desired composition.

It is carried on in a converter (Fig. 132). This is a huge, pear-shaped vessel, supported on trunnions so it can be tipped into different positions; one trunnion (*A*) is hollow, and at the bottom there are holes (*B, B*), through which a powerful blast of air can be blown. The converter is made of thick wrought iron plates and is lined with an infusible mixture, largely silica (sand, SiO_2) with a little clay.

When in use the converter is swung into a horizontal position, and fifteen to twenty tons of molten cast iron are run in, often directly from the blast furnace. The air blast is turned on, and the converter is swung back to a vertical position. As the air is forced in fine jets

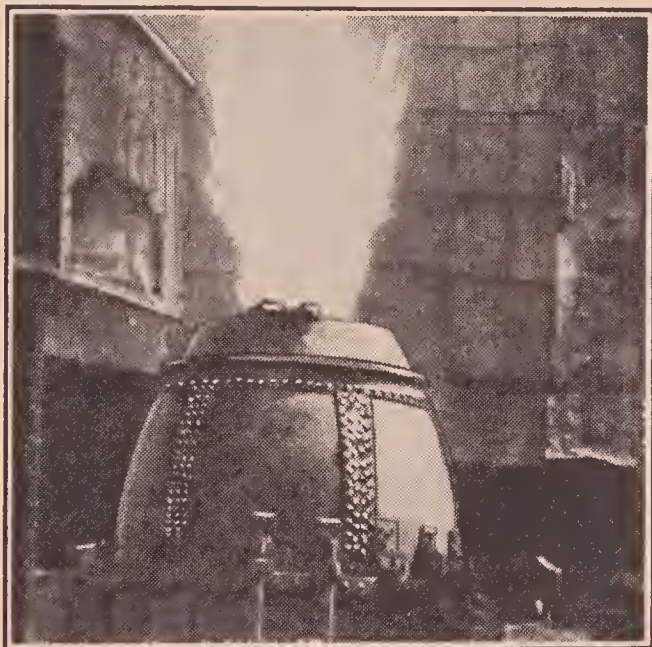


FIG. 133. — Making steel by the Bessemer process. Converter in operation.

through the molten metal, the temperature rises, and the carbon, silicon, and manganese that are in the iron are oxidized. The carbon forms carbon monoxide, which burns at the mouth of the converter in a large brilliant flame (Fig. 133), while the other oxides pass into the slag. This oxidation generates enough heat to keep the metal melted. In about fifteen minutes the diminished flame of burning carbon monoxide shows that the carbon has been oxidized and the other impurities removed. Then sufficient spiegel iron or ferro-manganese is added to the molten iron to furnish the proper amount of carbon (0.1 per cent for soft steel and 1.5 for hard, or 0.46 on the average) and manganese (about 0.9 per cent). By adding certain metals, *e.g.*,

aluminum, or iron alloys, *e.g.*, ferro-titanium or ferro-silicon, inclosed gases are removed (by reacting with the “deoxidizer” or “scavenger”), and a better quality of steel is produced.

After the completion of the whole operation the converter is tilted and the metal is poured into ladles, and then into molds to form blocks called ingots (Fig. 134, left foreground), which are subsequently shaped into rails or other objects.

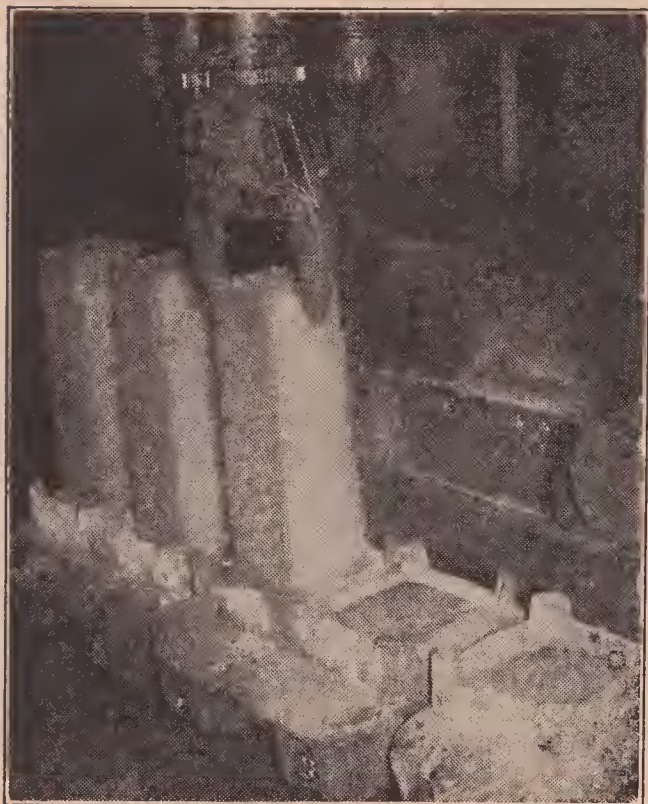


FIG. 134. — Ingots of steel.

The process described in the preceding paragraphs is called the **acid Bessemer process** because the converter is lined with silica, which is an acid anhydride (*i.e.*, the anhydride of silicic acid, H_2SiO_3). By (1) of this process the carbon and silicon can be removed but not all the sulfur and phosphorus. Both are objectionable. Sulfur makes steel brittle when hot, and phosphorus, when cold. The acid Bessemer process is used in the United States

because most domestic ores are low in phosphorus and sulfur.

But in Europe the Thomas-Gilchrist or basic process is used. The converter in this process is lined with burned dolomite (*i.e.*, practically a mixture of lime and magnesia, which are basic oxides), which removes the phosphorus and sulfur. This lining after use is known as Thomas slag. It is utilized as a fertilizer on account of its phosphorus (§ 300).

311. The open-hearth process. — This process is used extensively in the United States and yields over 75 per cent of the annual production. It consists in heating a mixture of cast iron, scrap iron, and iron oxide in a furnace lined with

a reacting material — burned dolomite or sand (see below). The process is conducted in a special kind of furnace called

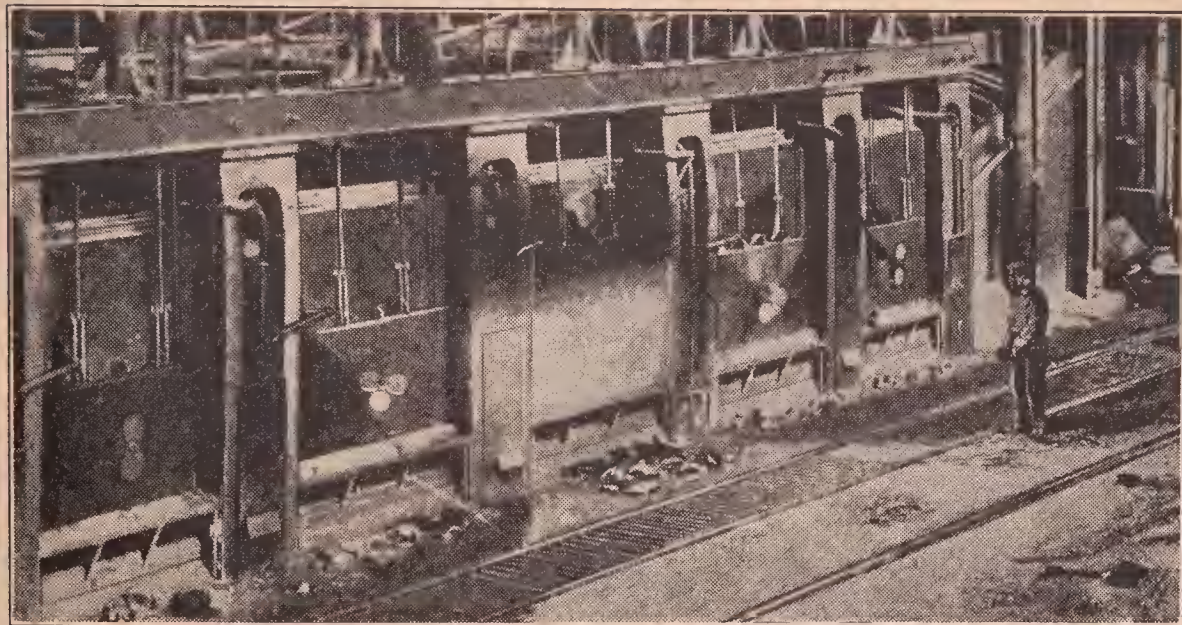


FIG. 135. — General view of a row of open-hearth furnaces.

an open-hearth furnace (Fig. 135). A vertical section is shown in Fig. 136. The depressed hearth (*H*), on which the charge is put, is lined with burned dolomite in the basic process and with sand in the acid process. A sloping roof of fire brick is just above the hearth. At the base of the furnace are duplicate chambers of checkerwork (*A* and *B*, *C* and *D*) arranged for alternate use.

To operate, fuel gas (or oil) is burned in a

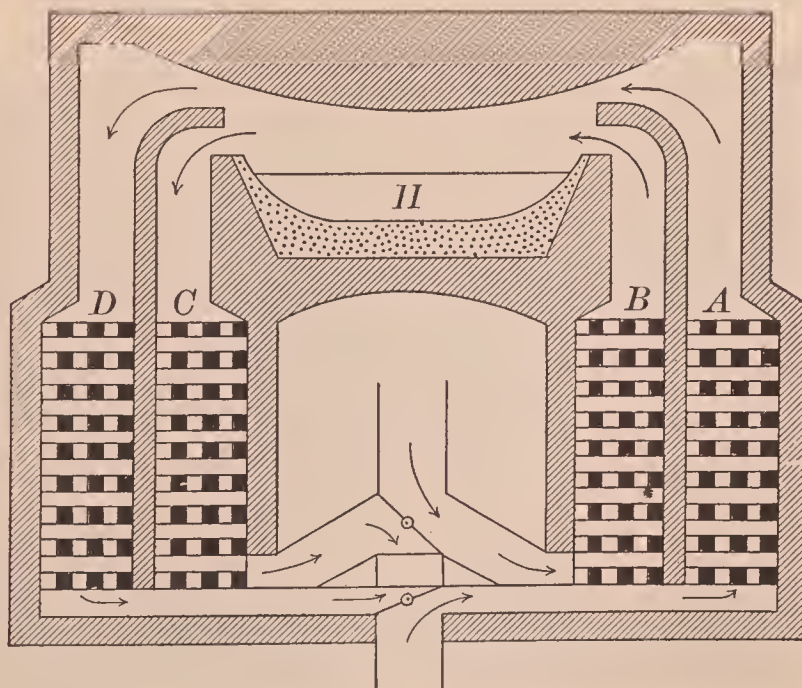


FIG. 136. — Sketch of an open-hearth furnace.

hot gases are passed through *A*, *B*, to the chimney, thus heating this checkerwork very hot. The hot gases are then passed

through *B* and air through *A*, and the two brought together over the hearth. Here the gas burns and produces a high



FIG. 137. — Pouring molten iron into an open-hearth furnace.

temperature on the hearth. Meanwhile the hot products of combustion and the unused gases, instead of escaping immediately up the chimney, are directed by valves through the other two chambers of the checkerwork *C*, *D*, and heat them. That is, while *A* and *B* are cooling, *C* and *D* are heating. At the proper time the fuel gas and air are shifted (by valves) to *C*, *D* and made to pass

through this checkerwork to the hearth and out over the other checkerwork (*A*, *B*) to the chimney.

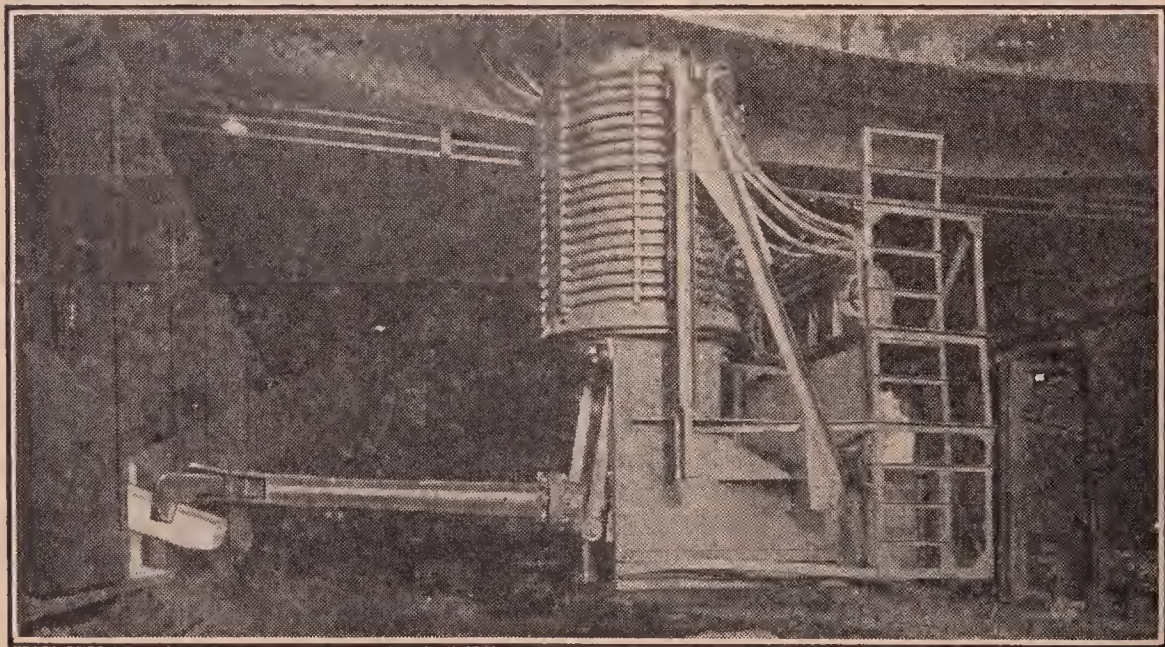


FIG. 138. — Putting an ingot of cast iron into an open-hearth furnace.

By this plan the process is alternated, one checkerwork being cooled as the other is heated, and vice versa. It is only

by this **regenerative process**, as it is called, that enough heat is obtained continuously to keep the charge melted as it becomes purer and purer.

The charge consists of 50 to 75 tons of cast iron and some iron oxide (*e.g.*, hematite); scrap iron, or steel, and lime are usually added (Figs. 137, 138). The carbon is largely oxidized to carbon dioxide, which escapes. The silicon, sulfur, and phosphorus are converted into oxides (acid oxides), which form a slag with the hearth lining (a basic oxide). The charge is heated



FIG. 139. — Drawing a sample of steel from an open-hearth furnace for a chemical test in the laboratory.

about eight hours. Samples are taken out at intervals (Fig. 139) and tested by the chemist. When tests show that the metal contains the desired proportion of carbon and other

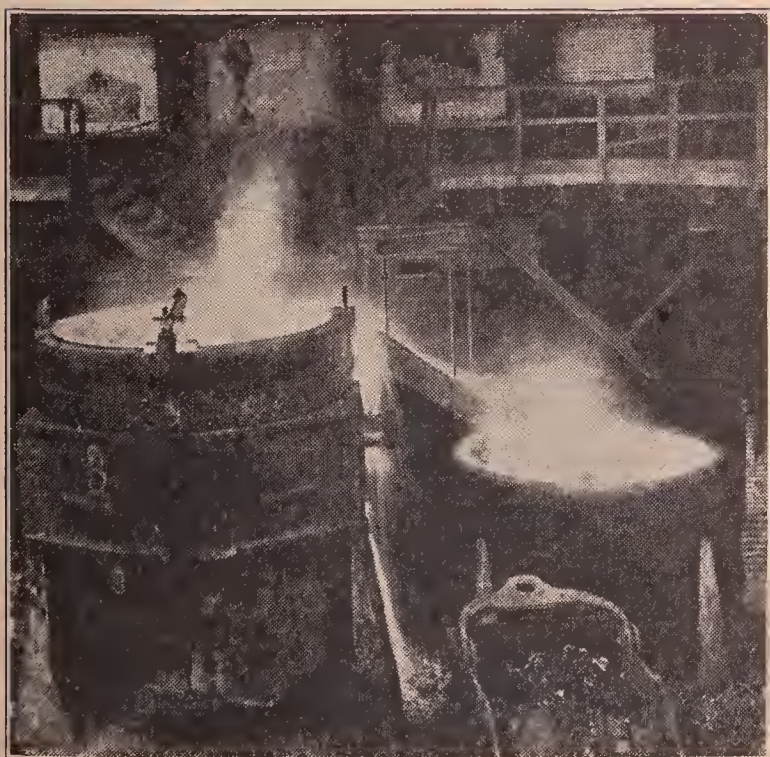


FIG. 140. — Tapping an open-hearth furnace.

constituents, the steel is tapped into ladles (Fig. 140), and certain materials are added, *e.g.*, aluminum or ferro-alloys of silicon, manganese, or titanium, to remove objectionable gases. It is then quickly poured into molds and allowed to cool into ingots (Fig. 134). Subsequently the ingots are softened by

reheating, and rolled, pressed, or stamped into desired shapes (Figs. 141, 142, 143).

The open-hearth process is replacing the Bessemer process because it is easily controlled, operates on a large scale, can be followed by tests, and yields a more uniform product of the desired composition.

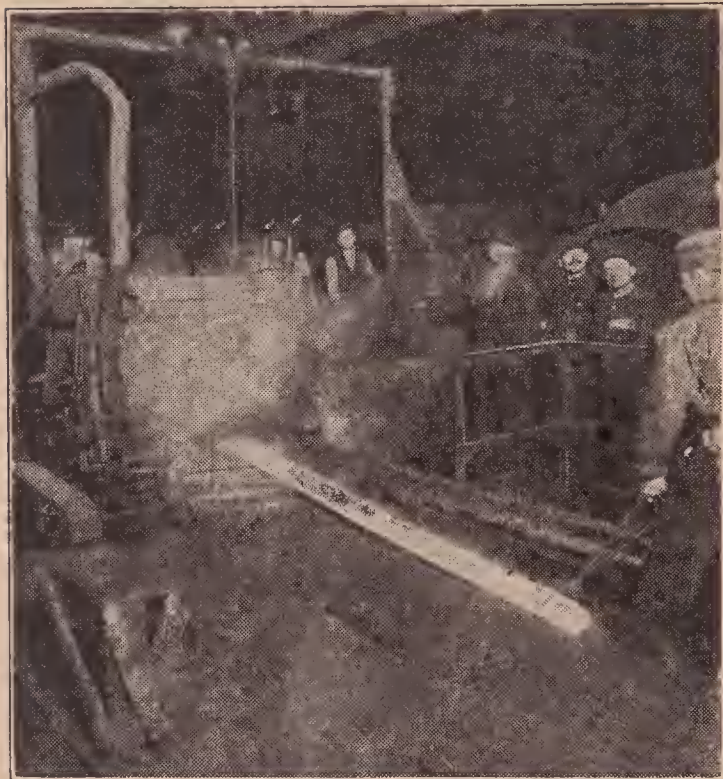


FIG. 141. — Making a steel rail — first stage.

Open-hearth steel is tough and elastic and is made into bridges, shafts, girders, heavy rails, large machines, large guns, and gun carriages.

312. The crucible process. — This consists in melting wrought iron, or low carbon steel, in crucibles made of graphite and clay. The charge varies with the product desired. For example, iron oxide may be added, or certain metals, such as chromium, vanadium, or molybdenum.

The crucibles are covered and then heated to a high temperature from four to five hours. During the heating the iron is slowly changed into steel by absorbing the proper proportions of carbon (0.75 to 1.5 per cent).

Crucible steel is very hard, and is used to make tools, razor blades, files, knives, springs, drills, dies, pens, and needles.

313. The electric process. — This process consists in heating a selected charge of cast iron or steel in an electric furnace (Fig. 144).

The heat is generated, usually, by the arc established between the carbon electrode and the melted charge. Very high temperatures are obtained. Moreover, the operation is conducted in a non-oxidizing atmosphere. Hence, the electric process is advantageously used in conjunction with the Bessemer and open-hearth processes to produce a superior steel free from sulfur and phosphorus.

314. Properties of steel. — The properties are numerous because there are many varieties of steel. Thus, steel, using this term broadly, is fusible and malleable, and can be forged, welded, and cast. Varieties containing 0.2 per cent

of carbon ("low carbon") are much like wrought iron and are called **soft or mild steel**. **Structural steel** contains more carbon (0.2 to 0.8 per cent) and is hard like cast iron, while **tool steel**, which contains upwards of 1.5 per cent of carbon ("high carbon"), is very hard indeed.

The properties of steel depend not only on the proportion of carbon (and other elements) but also on the special **heat treatment** which it receives. If steel containing the aver-

age per cent of carbon (0.90) is heated to about 800°C . and then suddenly cooled by plunging it into cold water or oil, it

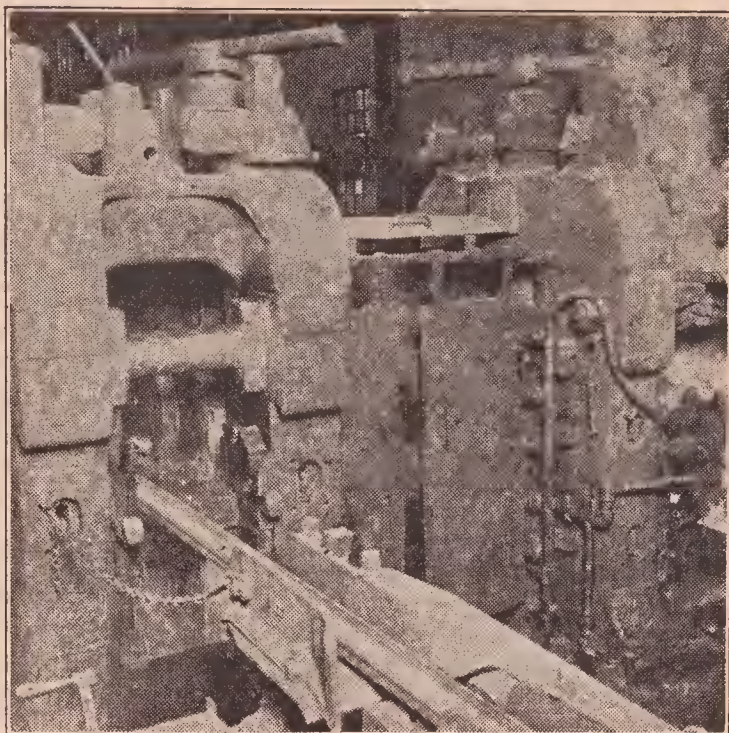


FIG. 142. — Making a steel rail — final stage.



FIG. 143. — Steel plate passing through the last rolling machine.

becomes brittle and very hard (Fig. 145). But if the same kind of steel is heated and then cooled slowly, it becomes tough, elastic, and soft enough to be filed. All grades of hardness can be obtained between these two extremes. Thus, if hardened steel is reheated to a definite temperature, determined approximately by the color the oxidized metal assumes, and then properly

cooled, almost any degree of hardness and elasticity can be obtained. This last operation is called **tempering**.

315. Special steels. — Special steels, or steel alloys as they are sometimes called, are made by melting a definite

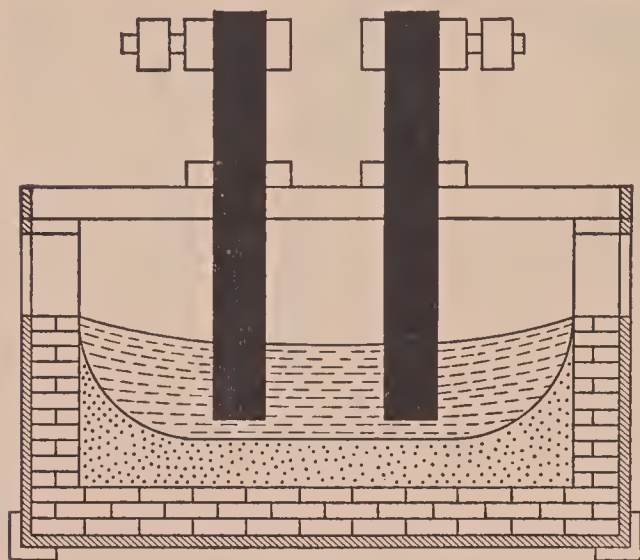


FIG. 144. — Sketch of an electric furnace for the manufacture of steel.

proportion of certain metals, or their ferro-alloys, into steel. These special steels have properties which fit them for indispensable uses.

1. Nickel steel containing up to 3.5 per cent nickel is hard, tough, and resists corrosion. It is used for armor plate, cables, drills, bridge trusses, propeller shafts, and marine engine parts.

Steel containing 30 to 40 per cent of nickel resists corrosion so effectively it is made into pumps used for salt water. The alloy containing 36 per cent of nickel expands or contracts so very slightly it is made into surveyor's tapes, pendulums, and scientific ap-

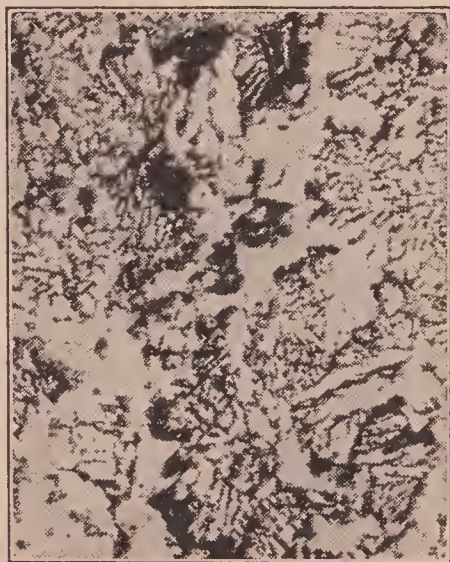


FIG. 145. — Photomicrographs of hard steel (right) and cast steel (left). (Compare Fig. 131.)

paratus. It is called **invar**. The alloy containing about 42 per cent of nickel expands and contracts to the same extent as platinum. It is used in making wire glass and as

the leading-in wires of electric light bulbs instead of the scarce and expensive metal platinum. It is called **platinite**.

2. Chromium steels, made by adding the alloy ferrochrome to molten steel, contain from 1.5 to 2 per cent of chromium. They are very hard and are used for armor-piercing projectiles, safes, and crushing machinery. If small proportions of other metals are added, such as nickel, vanadium, and manganese, the steels are unusually tough, elastic, and hard. They resist shocks and strain, and are used in making automobile frames and axles.

3. Tungsten steels are hard, and if of the right composition, do not lose their hardness at a red heat. A typical one contains 18 per cent of tungsten, 3.5 per cent of chromium, and a small fraction of a per cent of vanadium. They are called **high speed steel** and are used to make tools for cutting metals. These tools, unlike the usual tool, do not lose their edge when heated but will cut when they are dull red from the heat produced by friction. Molybdenum sometimes replaces tungsten, and much less is needed to produce the same results as with tungsten.

4. Manganese steels, containing 7 to 20 per cent of manganese, or about 13 per cent on the average, are extremely hard without being brittle. They are used for making the jaws of rock-crushing machinery, steam shovels, dredger buckets, safes, parts of brakes, and rails (especially railroad rails for curves).

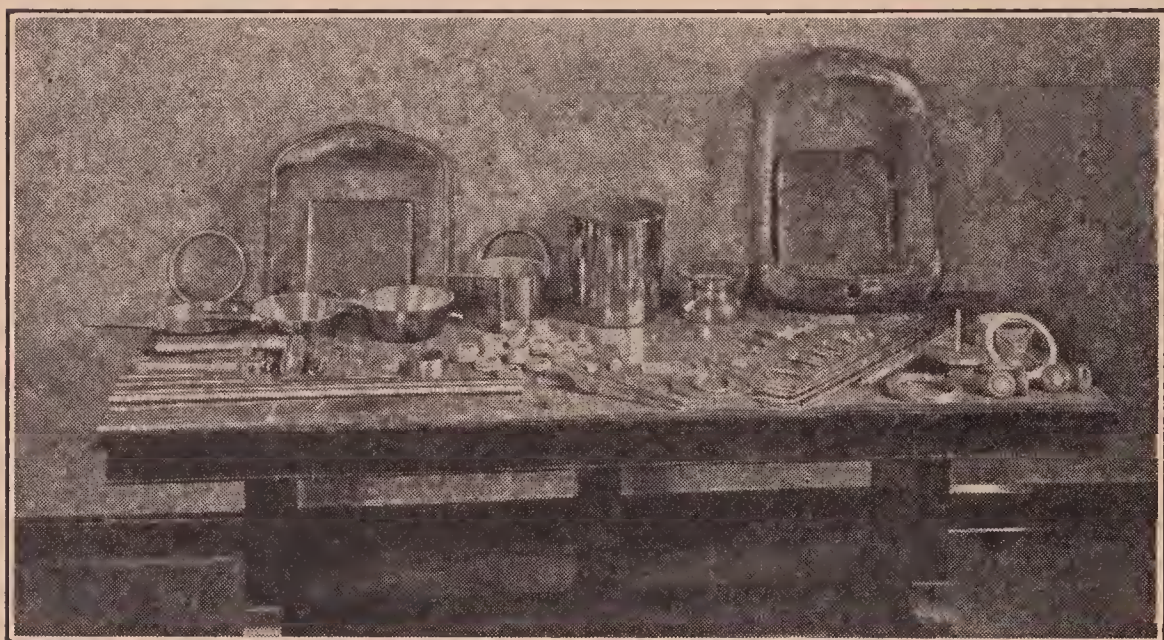
Stainless "steel," or stellite, is not steel at all, but an alloy of chromium (15 to 35 per cent), cobalt (50 to 75), and small per cents of iron, carbon, and tungsten. It does not rust, or even stain, and is used to make cutlery and surgical instruments.

316. Rusting. — Iron and steel rust readily in moist air, *i.e.*, they gradually change into a brittle, porous, loosely adherent brown solid. This solid, which is called **iron rust**, varies in composition, though it is often considered as essentially hydrated ferric oxide ($3 \text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or $2 \text{Fe}_2\text{O}_3 \cdot 3 \text{H}_2\text{O}$).

Rusting is a complex process and is explained in different ways. An acceptable interpretation is based on the ionic theory. The iron goes into solution as ferrous ions (Fe^{++}).

Hydrogen ions (H^+) from the water lose their charges and become atoms; the atoms unite to form molecules which escape as hydrogen gas (H_2). The ferrous ions combine with the hydroxyl ions (OH^-) left in the water, thereby forming ferrous hydroxide ($Fe(OH)_2$), which is subsequently converted into the complex substance called iron rust. Once begun, rusting proceeds rapidly, because the film of rust is not compact enough to protect the metal.

The loss from rusting is enormous. Various methods have been devised to prevent it. One is to expose the hot metal



Courtesy Central Alloy Steel Co.

FIG. 146. — Objects made of rustless iron.

to steam until a thin film of magnetic oxide (Fe_3O_4) forms on the surface. This film adheres firmly and prevents rusting to a large extent. Iron so coated is often called Russia iron.

Another method is to paint the metal first with red lead paint and then with some less conspicuous kind. Sometimes, special black paints or aluminum (powder) paint are used, the latter having special value as a coating for oil storage tanks.

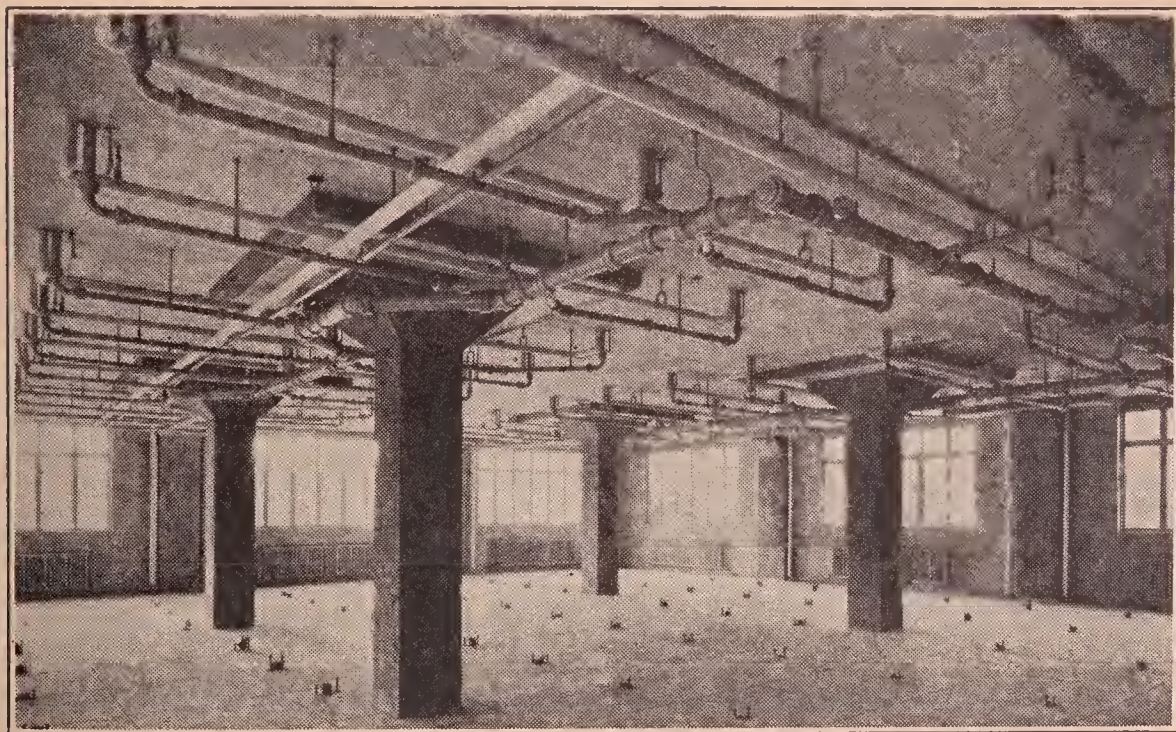
Sometimes an enamel coating is melted upon the metal. This process is used in making kitchen utensils.

Iron is often "tinned," *i.e.*, sheets of iron or "low carbon" steel are carefully cleaned and dipped into melted tin.

Tinned iron, or tin plate as it is often called, does not rust until the tin is worn off, and then the rusting proceeds rapidly.

Another metallic coating largely used is zinc. The iron is cleaned and dipped into melted zinc. The product is called **galvanized iron**. It is extensively used for wire, netting, roofs, pipes, cornices, and water tanks.

Special alloys of iron called rustless iron are a recent product (Fig. 146). One contains about 14 per cent of silicon.



Courtesy Duriron Co. Inc.

FIG. 146a. — Duriron waste pipe on the ceiling of a chemical laboratory for draining the sinks on the floor above.

It is called duriron. It is used in acid plants and as the waste pipe in laboratories (Fig. 146a).

317. Two series of iron compounds. — Iron forms two series of compounds — ferrous and ferric. Corresponding members differ in properties. In each series the iron plays a different rôle. The valence of iron is $+2$ in ferrous compounds and $+3$ in ferric. Ferrous salts in solution give ferrous ions (Fe^{++}) and ferric salts give ferric ions (Fe^{+++}).

Ferrous compounds are readily oxidized into the corresponding ferric compounds. For example, *ferrous* chloride in hydrochloric acid solution becomes *ferric* chloride in the presence of an oxidizing agent, such as nitric acid or potassium

permanganate. Whereas ferric compounds are readily reduced to ferrous compounds. Thus, ferric chloride becomes ferrous chloride by the action of hydrogen sulfide, sulfurous acid, or stannous chloride (SnCl_2). So also ferrous chloride becomes ferric chloride by action with chlorine, while ferric chloride becomes ferrous chloride by action with iron, thus : —



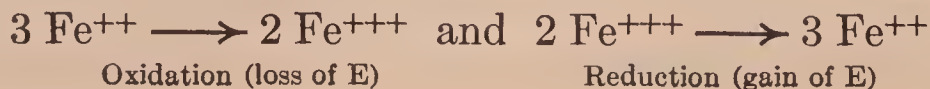
That is to say, the change from a ferrous to a ferric compound is the same type of change as from sulfurous acid to sulfuric acid. It is an example of oxidation, while the reverse is reduction. Oxygen need not be involved. We often use the terms *oxidation* and *reduction* in a broader sense than mere addition and removal of the element oxygen.

Let us interpret the broader meaning of these terms. Oxygen belongs to the class of negative elements. So does chlorine. Now if we add chlorine to ferrous chloride, we are doing chemically just what we do if we add oxygen to sulfurous acid, *viz.*, oxidizing. In a broad sense, then, oxidation is the process of adding oxygen, chlorine, or another negative element. Conversely, reduction is the process of removing oxygen, chlorine, or another negative element.

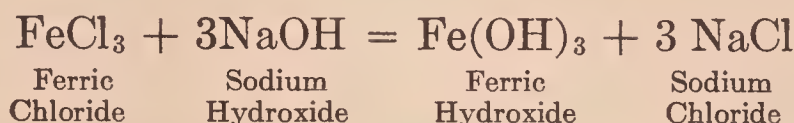
As stated above, the valence of iron is + 2 in ferrous and + 3 in ferric compounds. In passing from ferrous to ferric compounds the valence of the iron increases; and conversely, from ferric to ferrous it decreases. From the standpoint of valence, **oxidation** is an increase in the valence of an element, whereas **reduction** is a decrease.

Furthermore, since dissolved iron salts pass readily from one series to the corresponding members of the other, oxidation is sometimes called the gain of a positive charge, *e.g.*, Fe^{++} to Fe^{+++} , whereas reduction is the loss of a positive charge, *e.g.*, Fe^{+++} to Fe^{++} .

Still another way to describe oxidation and reduction is in terms of electrons (§§ 357, 358, 424, 529). Oxidation is the loss and reduction the gain of electrons, thus : —



318. Iron hydroxides. — The white solid formed by the interaction of a ferrous salt and an hydroxide is **ferrous hydroxide** ($\text{Fe}(\text{OH})_2$). Exposed to the air, it soon turns green, and finally brown, owing to oxidation to ferric hydroxide. **Ferric hydroxide** ($\text{Fe}(\text{OH})_3$) is a reddish brown solid, formed by the interaction of a ferric salt and an hydroxide, thus : —



319. Ferrous sulfate. — This is a green salt obtained by the interaction of iron (or of ferrous sulfide) and dilute sulfuric acid. It is manufactured by roasting (*i.e.*, oxidizing) iron pyrites (FeS_2), or by exposing pyrites to moist air; the mass is extracted with water containing scrap iron and a little sulfuric acid. Considerable is obtained in “pickling” iron castings with dilute sulfuric acid. The large light green crystals ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) are called **green vitriol or copperas**.

Large quantities are used in dyeing silk and wool, as a disinfectant, and in manufacturing ink, bluing, and pigments. Much black writing ink is made essentially by mixing ferrous sulfate, nutgalls, gum, and water. A mixture of ferrous sulfate and lime is sometimes used to purify water and sewage by the settling process (§ 81).

320. Ferrocyanides and ferricyanides. — The most important are potassium ferro- and ferricyanides. **Potassium ferrocyanide** ($\text{K}_4\text{Fe}(\text{CN})_6$) is a lemon-yellow solid. The crystallized salt contains three molecules of water of hydration. It is sometimes called **yellow prussiate of potash**. Unlike the simple cyanogen compounds (*e.g.*, HCN and KCN), it is not poisonous. **Potassium ferricyanide** ($\text{K}_3\text{Fe}(\text{CN})_6$) is a dark red crystallized solid (without water of hydration). It is often called red prussiate of potash.

321. Making a blue print. — Blue print paper is prepared by coating paper with a mixture of potassium ferricyanide and ammonium ferric citrate solutions, and drying in a dark place. In the sunlight the ferric salt is partly reduced and forms a bronze-colored deposit by interaction with the potassium ferricyanide.

If such prepared paper is covered with a photographic negative, or with transparent cloth marked with lines in black ink, and exposed to the sun or an electric light, the paper is acted upon only in the exposed places. Upon washing, the exposed parts become blue, and the covered parts white — hence the name “blue print.”

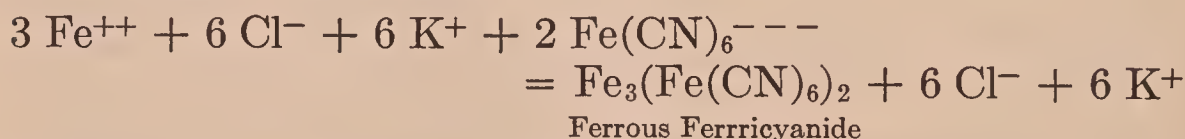
322. Tests for ferrous and ferric compounds. — Solutions of ferrous salts and potassium ferricyanide interact and precipitate **ferrous ferricyanide** ($\text{Fe}_3(\text{Fe}(\text{CN})_6)_2$). This is a dark blue solid, called **Turnbull's blue**. Ferric salts interact with potassium ferrocyanide and precipitate ferric ferrocyanide ($\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$). This precipitate is likewise dark blue and is called **Prussian blue**. By these tests ferrous and ferric salts can be distinguished. Hence to test for —

Ferrous salts add potassium ferricyanide,
Ferric salts add potassium ferrocyanide.

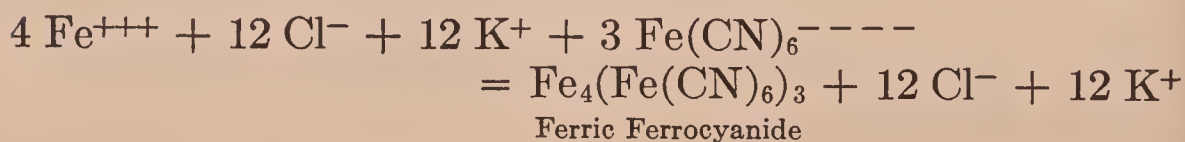
In each test we obtain a dark blue precipitate, but only if we use “ferrous with ferri-” and “ferric with ferro-.”

Besides the above tests for ferric salts, potassium thiocyanate (KCNS) produces a red solution of ferric thiocyanate ($\text{Fe}(\text{CNS})_3$) with ferric salts, but leaves ferrous salts unchanged.

Since these two “blue” tests are apt to confuse, let us interpret them. Ferrous salts in solution yield ferrous ions (Fe^{++}). Potassium ferricyanide in solution yields potassium ions (K^+) and ferricyanide ions ($\text{Fe}(\text{CN})_6^{---}$). When ferrous chloride and potassium ferricyanide solutions are mixed, ferrous ions unite with ferricyanide ions and form ferrous ferricyanide, thus: —



Similarly, ferric chloride and potassium ferrocyanide react thus: —



The dark blue precipitate is formed only by the combination of either (1) ferrous and ferricyanide ions or (2) ferric and ferrocyanide ions.

EXERCISES

1. Describe the manufacture of cast iron.
2. Apply Exercise 1 to wrought iron.
3. State the physical properties of (a) cast iron and (b) wrought iron.
4. Describe the manufacture of steel by (a) the Bessemer process, (b) the open-hearth process, (c) the crucible process, and (d) the electric process.
5. How are ferrous compounds changed into ferric compounds, and vice versa? Give equations.
6. Write the formulas of (a) the ferrous and (b) the ferric salts of the following acids: carbonic, nitric, sulfuric, orthophosphoric (H_3PO_4).
7. Complete and balance the following: (a) $\text{FeCl}_2 + (\text{NH}_4)_2\text{S} = \text{FeS} + \text{---}$; (b) $\text{FeCl}_3 + \text{---} = \text{Fe}(\text{OH})_3 + \text{NH}_4\text{Cl}$; (c) $\text{Fe} + \text{O} = \text{Fe}_2\text{O}_3$; (d) $\text{K}_3\text{Fe}(\text{CN})_6 + \text{---} = \text{---} + \text{K}_2\text{SO}_4$; (e) $\text{K}_4\text{Fe}(\text{CN})_6 + \text{---} = \text{---} + \text{KCl}$.

PROBLEMS

(See Problems at the end of Chapters VIII, IX.)

1. Calculate the weight of iron in 70 tons of hematite (95 per cent pure).
2. What is the simplest formula of a compound, if 9 gm. of it yielded 4.8 gm. of sulfur and the rest iron?

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

- Exercise 59 — Tests for Iron Salts.
 Exercise 60 — Reduction and Oxidation of Iron Salts.
 Exercise S5 (a) — Slow Oxidation — T.
 Exercise *2 — Mixture and Compound.

SUPPLEMENTARY SECTIONS FROM PART II

At this point sections may be selected from Topics XXII (Copper), XXIII (Magnesium — Zinc — Mercury), XXIV (Silver — Photography — Gold), XXV (Aluminum — Clay Products), XXVI (Lead), XXVII (Radium — Radioactivity).

BRIEF COURSE IN CHEMISTRY

PART II

SUPPLEMENTARY TOPICS

SUITABLE FOR SPECIAL NEEDS AND
FOR ADDITIONAL STUDY

SUPPLEMENTARY TOPICS

TOPIC I: ELEMENTS — ENERGY — CHEMICAL CHANGE

325. Distribution of the elements. — Approximately 98 per cent of the outer shell (about ten miles deep) of the earth's crust consists of compounds of only eight elements. The per cent of these elements is shown in Table VIII.

TABLE VIII. — PER CENT OF COMBINED ELEMENTS
IN THE EARTH'S CRUST

Oxygen . . .	46.71	Iron	5.05	Potassium . .	2.58
Silicon . . .	27.69	Calcium . . .	3.65	Magnesium . .	2.08
Aluminum . .	8.07	Sodium . . .	2.75	Remainder . .	1.42

Compounds in the ocean contain only a few elements, as seen by Table IX.

TABLE IX. — PER CENT OF COMBINED ELEMENTS IN
THE OCEAN

Oxygen . . .	85.79	Sodium . . .	1.14	Calcium . . .	0.05
Hydrogen . .	10.67	Magnesium . .	0.14	Bromine . . .	0.008
Chlorine . . .	2.07	Sulfur	0.09	Carbon	0.002

The atmosphere contains about 21 per cent of oxygen, 78 of nitrogen, and 1 of argon — all as free elements.
The human body, complicated as it is, consists mainly of compounds of about six elements together with as many more elements in very small proportions, some only in traces (Table X).

TABLE X. — PER CENT (AVERAGE) OF COMBINED ELEMENTS IN THE HUMAN BODY

Oxygen . . .	65.00	Phosphorus . .	1.00	Magnesium . .	0.05
Carbon . . .	18.00	Potassium . .	0.35	Iron . . .	0.004
Hydrogen . .	10.00	Sulfur . . .	0.25	Iodine . . .	trace
Nitrogen . .	3.00	Sodium . . .	0.15	Fluorine . .	trace
Calcium . .	2.00	Chlorine . . .	0.15	Silicon . . .	trace

326. A good example of a chemical change. — If we light a candle and let it burn, the candle wax slowly disappears — “burns away.” By holding a cold, dry bottle over the burn-

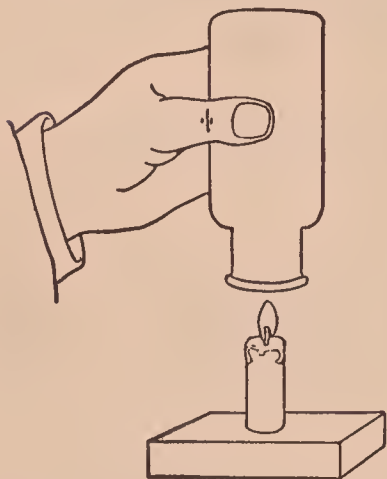


FIG. 147. — Studying the chemical change in a burning candle.

ing candle (Fig. 147), a film of water gathers on the inside. Now if we remove the bottle, pour in some calcium hydroxide (limewater), and shake the bottle, the clear liquid becomes cloudy, owing to the formation of fine particles of calcium carbonate. These were formed by a chemical change between the added calcium hydroxide and the carbon dioxide (produced by the burning candle). Hence, the candle wax did not really “burn away.” By burning in the air, the wax changed into water and carbon dioxide.

327. Energy and chemical change. — One striking feature of the experiment in which iron and sulfur are heated can not escape observation. That is, the reaction, once started by heat, proceeds with the evolution of a great deal of heat. In this experiment part of the chemical energy in the iron and the sulfur was transformed into heat. All chemical reactions, of course, do not result in the conspicuous evolution of heat, indeed in many reactions heat is absorbed, but every chemical change involves some change in energy. So we say: —

A characteristic of chemical change is the transformation of chemical energy into heat energy, or light energy, or both, and sometimes into electrical energy.

TOPIC II: THE METRIC SYSTEM

328. The metric system. — The fundamental unit of this system is the **meter**. It is the unit of length and is 39.37 inches. The meter and the other units have multiples and submultiples, which are designated by prefixes attached to the particular unit. Thus, kilo- is equivalent to 1000, and deci-, centi-, and milli- to 0.1, 0.01, and 0.001. Hence: —

10 millimeters (mm.) = 1 centimeter (cm.)

10 centimeters = 1 decimeter (dm.)

10 decimeters = 1 meter (m.)

In chemistry, the measures of length usually used are the millimeter (mm.) and centimeter (cm.); occasionally they

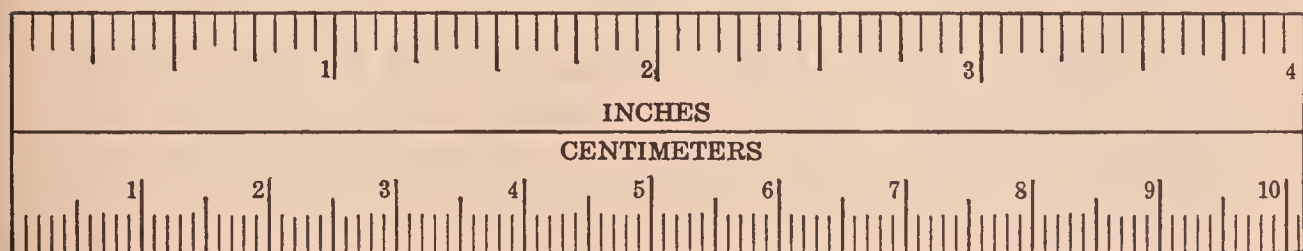


FIG. 148. — Comparative scale — metric below, English above. On the metric scale the numbered divisions are centimeters and the smallest are millimeters.

meter (m.) is used. A comparative scale (metric and English) is given in Fig. 148. Note that 2.5 cm. = 1 in. (very nearly). For convenience we might remember that a five cent piece is 2 centimeters in diameter and a worn ten cent piece is 1 millimeter thick.

The unit of weight is the **gram**. It is the one-thousandth part of a standard weight called the **kilogram**. Thus: —

10 milligrams (mg. or mgm.) = 1 centigram (cg. or cgm.)

10 centigrams (cg. or cgm.) = 1 decigram (dg. or dgm.)

1000 grams (gm.) = 1 kilogram (kg. or kgm.)

A kilogram weighs about 2.2 pounds (avoir.). Large weights are often expressed in kilograms (and a decimal fraction). A gram weighs 15.43 grains, or also nearly one thirtieth of one ounce (1 ounce = 28.55 grams). Small weights are expressed in grams and a decimal fraction. Thus,

2 grams, 2 centigrams, and 5 milligrams is written 2.025 grams (or gm.). A pint of water weighs a little less than 500 grams. A five cent piece weighs 5 grams.

The unit of volume is the **liter**. It is equal to the capacity of the vessel containing a kilogram of water. A liter equals about one quart. The table is: —

1000 cubic millimeters = 1 cubic centimeter (cc).

1000 cubic centimeters = 1 cubic decimeter (cu. dm.)

1 cubic decimeter = 1 liter (l.)

In chemistry the cubic centimeter and the liter are the denominations used to measure and express volume. Thus, a test tube measuring 15×1.8 cm. holds about 30 cc., a large test tube (20×2.5 cm.) holds about 75 cc., and the large greenish glass acid bottles hold 2.5 l.

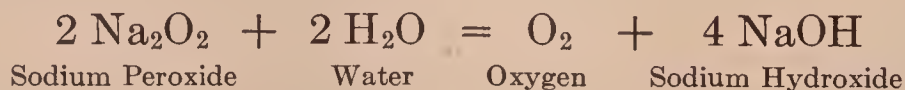
An approximate relation which can be used for water (and other liquids of the same specific gravity) is 1 liter = 1 kilogram = 1 cubic decimeter = 1000 cubic centimeters = 1000 grams = 2.2 pounds (avoirdupois).

TOPIC III: OXYGEN

329. Preparation of oxygen from various substances. — Oxygen can be prepared from other compounds besides potassium chlorate.

(1) Mercuric oxide (HgO), barium dioxide (BaO_2), lead dioxide (PbO_2), and lead tetroxide (Pb_3O_4), if heated separately, liberate oxygen and may be used to prepare the gas in the laboratory.

(2) When water is dropped slowly upon sodium peroxide (Na_2O_2), oxygen is liberated. The experiment must be done on a small scale. The equation is: —



(3) A mixture of hydrogen peroxide (H_2O_2), sulfuric acid, and potassium permanganate (KMnO_4) solution yields oxygen.

330. Lavoisier's famous experiment on combustion. — Lavoisier showed that oxygen is necessary for combustion.

He put mercury in a retort having a long neck which communicated with a jar (Fig. 149). The jar contained air confined over mercury (in the lower vessel). He heated the retort and kept the mercury in the retort just below the boiling point for twelve days. When the apparatus was cold, he noticed two things: (1) A red substance had accumulated on the surface of the mercury in the retort, and (2) the air in the retort and jar had decreased in volume about one fifth.

He picked off the red substance, heated it intensely, collected the liberated gas, and measured its volume. It was

the same as the decrease in the volume of the original air inclosed in the apparatus. He tested this gas, and found it had the properties of the gas previously obtained by Priestley, especially the property of making a lighted candle burn vigorously. He also tested the gas left behind in the retort and jar and noted that it extinguished a lighted

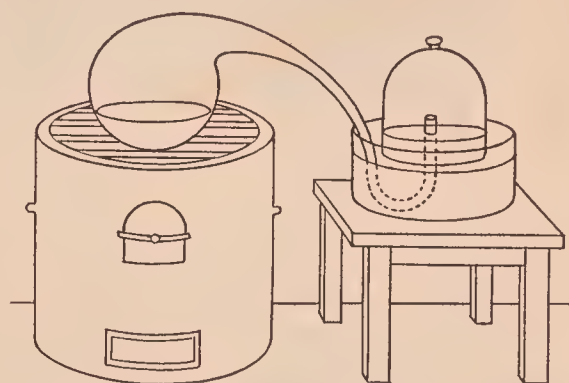


FIG. 149. — Apparatus used by Lavoisier in his famous experiment on combustion.

candle. From these facts Lavoisier concluded: (1) air contains a gas which is removed by heating substances in it, (2) this gas is about one fifth of air, (3) this gas unites with substances in the process called combustion or burning, and (4) this gas is identical with the gas (*i.e.*, oxygen) obtained by Priestley from his "red precipitate of mercury."

331. Oxidation and energy. — During oxidation, some of the chemical energy of the oxygen and the other substances is transformed into heat energy and often into light energy. Oxidation takes place at different rates. But the actual amount of heat energy liberated in a single case of oxidation is the same, whether the oxidation is slow or rapid (§ 333). To be sure the temperature resulting from slow oxidation is much lower than from rapid oxidation. But temperature, as registered on a thermometer, tells "how hot" a substance

is. Quantity, *i.e.*, “how much” heat, is measured in a calorimeter (§ 384) and is stated in calories. A small **calorie** (cal.) is the amount of heat required to raise the temperature of one gram of water one degree centigrade (usually from 15° to 16° C.).

TOPIC IV: CARBON

332. How coal was formed.—Ages ago the vegetation was exceedingly dense and luxuriant upon the land slightly

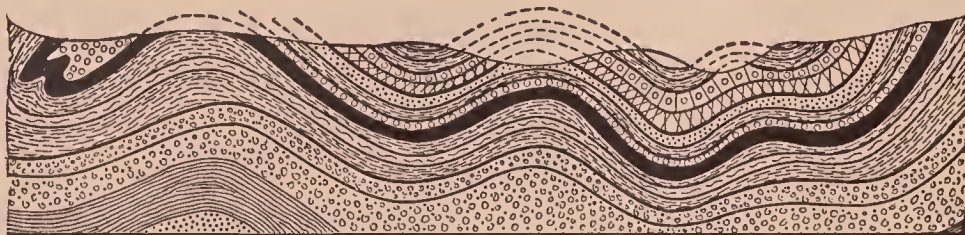


FIG. 150. — Section of the earth's crust showing layers of coal.

raised above the sea. In process of time this vegetation decayed, accumulated, and became covered with sand, mud, and water. The vegetable matter was slowly changed by heat and pressure into impure carbon. These geological and chemical changes were repeated, and as a result there



FIG. 151. — Fossil found in a coal bed.

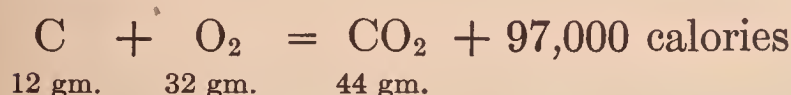


FIG. 152. — Section of coal as seen through a microscope.

are in the earth layers or seams of carbonaceous matter varying in thickness and composition (Fig. 150). These are the

coal beds. Coal beds contain proofs of their vegetable origin, *viz.*, impressions of vines, stems, and leaves of plants, and similar vegetable substances (Fig. 151). A thin section of coal examined through a microscope shows a vegetable structure (Fig. 152).

333. Carbon and energy. — Careful experiments made in a calorimeter (§ 384) show that the same amount of heat, stated in calories (§§ 235, 383), is produced in a given oxidation reaction, provided, of course, the same weight and kind of product is formed in each case by oxidizing a certain weight of substance. For example, 12 gm. of carbon (charcoal) form 44 gm. of carbon dioxide. Now this weight of carbon (12 gm.) in burning liberates 97,000 calories, whether we burn it slowly or rapidly. The thermo-chemical equation for this reaction is: —



This equation may be interpreted as follows: When carbon and oxygen react, carbon is oxidized; some of the chemical energy in these substances is transformed into heat energy; and 97,000 calories are liberated for every 12-gram portion of carbon which is oxidized.

334. Carbon dioxide and plants. — The fact that plants take up carbon dioxide and reject oxygen can be readily illustrated.

Fresh green leaves are put into the flask (Fig. 153), which is then completely filled with water saturated with carbon dioxide. The stopper with its funnel is pushed in to exclude the air, the funnel is partly filled with the same liquid, and the test tube is filled and arranged as shown in the figure. On exposure to the sunlight for several hours, a gas collects in the test tube. The usual test shows that the gas is oxygen.

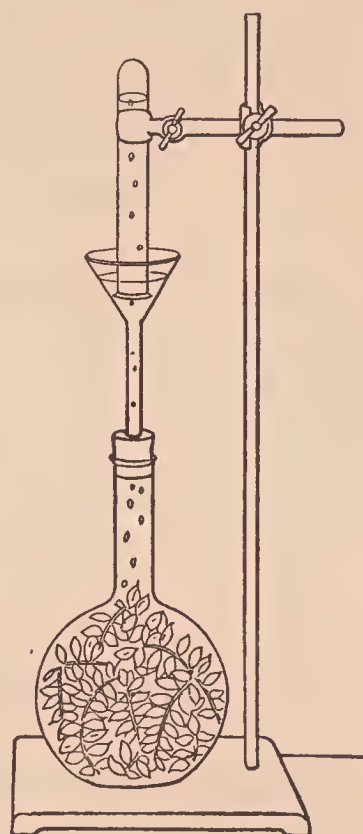


FIG. 153. — Experiment showing the absorption of carbon dioxide and liberation of oxygen by plants.

TOPIC V: HYDROGEN

335. Hydrogen and energy. — The burning of hydrogen in oxygen involves the transformation of a large amount of chemical energy into heat energy. Thus, 1 gm. of hydrogen in burning to water (vapor) yields 29,050 calories; if the resulting water vapor is condensed to the liquid form, then about 34,000 calories are liberated. This is a large amount of heat energy. One gram of carbon, for example, gives only about 8000 calories (§ 333). The thermo-chemical equation may be written in full thus: —



336. Hydrogenation of fats. — Liquid fats (usually called oils) are mixtures of several fats. One of the ingredients is a liquid called olein. It contains 2 hydrogen atoms less in a molecule than the solid fat stearin. The chemical change hastened by the catalyst is the chemical addition of 2 hydrogen atoms to each molecule of olein.

TOPIC VI: GASES AND THEIR MEASUREMENT

337. Gases. — Gases are sensitive substances. They contract and expand with the slightest change in temperature or pressure. Hence the volume of a gas changes readily.

338. Measuring gases. — In chemistry we often need to know the weight of a certain volume of a gas, *e.g.*, 1 liter, or 22.4 liters, of a gas, or to compare the weights of the same volume of different gases. But since gases change so readily in volume, we can not compare weights of different gases unless the volumes are measured at the same temperature and pressure.

We can find the volume of a gas by measuring the capacity of the container; or we can conduct the gas into vessels on which the capacity is marked in some conspicuous way (Fig. 154). We can measure volumes very accurately. And if we find (or know) the volume of a sample of a gas, we can find its weight by calculation (§ 345).

339. Finding the volume of a gas. — As already stated, the volume of a gas changes readily with variations of temperature and pressure. This means that the actual volume of a definite weight of gas depends on the temperature and pressure prevailing at the time the volume is read. Hence, to give an accurate meaning and value to the measurement of a gas volume we must specify the exact temperature and pressure at which the measurement was made.

By agreement among scientists, the **normal or standard temperature** is 0°C. , *i.e.*, zero degrees on the centigrade thermometer, and the **normal or standard pressure** is 760 mm., *i.e.*, the pressure when the mercury column of a barometer is 760 millimeters high. These conditions of temperature and pressure (0°C. and 760 mm.) are called **standard conditions**. Under these conditions a liter of dry oxygen gas, for example, weighs 1.429 gm. But at another temperature or pressure the weight of oxygen gas filling a liter vessel would be different. Thus, if the pressure is increased, the volume becomes less, more gas must be added to bring the volume up to a liter, and this total quantity of oxygen would weigh more than 1.429 gm. That is, a liter vessel, when full, contains a liter, but the weight of the contents varies with the quantity of gas in the vessel.

If we could measure gases at 0°C. and 760 mm., their volumes could be compared directly, and the weights deduced or obtained directly from these volumes would be a true measure of the actual quantity of the gases in the observed volumes. But it is not convenient to measure gases at 0°C. and 760 mm. So it is customary to measure the volume at the temperature and pressure prevailing at the time of the experiment, and then *compute what the observed volume would occupy if it were under standard conditions*. This mathematical process is possible because two laws define the behavior of gases under variation of temperature and pressure. These laws are the law of Charles and the law of Boyle.



FIG. 154. — Graduated tube for measuring the volume of a gas.

340. The relation between volume and temperature, and the law of Charles. — Gases expand when heated and contract when cooled. The change in volume is the same for all gases, provided there is no change in pressure. Thus, at constant pressure a gas at 0°C ., if warmed to 1°C ., will expand $\frac{1}{273}$ of the volume it occupied at 0°C . And for each

CENTIGRADE ABSOLUTE

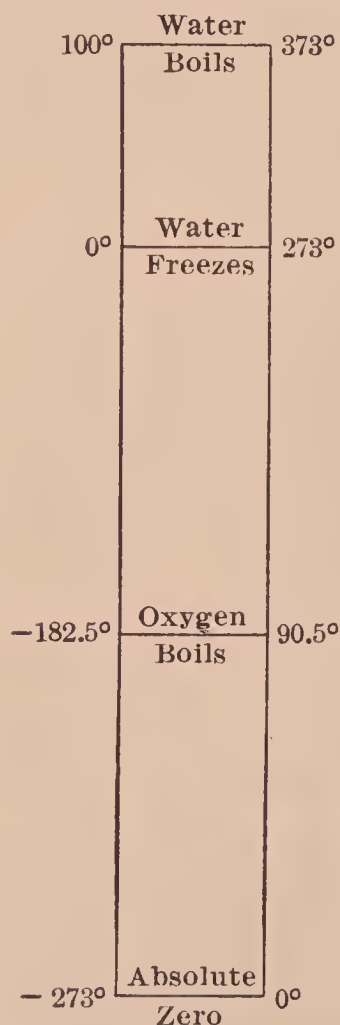


FIG. 155. — Centigrade and absolute scales.

additional rise of 1°C ., the volume will increase $\frac{1}{273}$ of the volume at 0°C . Conversely, if a gas at 0°C . is cooled to -1°C ., it will contract $\frac{1}{273}$ of its volume, and for each additional fall of 1°C . there will be a decrease of $\frac{1}{273}$ of the volume at 0°C .

At this rate of contraction a gas would have no volume at -273°C .! But this rather startling result does not actually happen, because all gases become solids before the temperature reaches -273°C . Nevertheless for convenience we use this point (-273°) on the centigrade thermometer as the starting point of another temperature scale called the absolute temperature. The temperature -273°C . is called **absolute zero**, and the temperatures reckoned from this point as zero are called **absolute temperatures**. If an "absolute thermometer" were constructed with divisions equal to those on the centigrade scale and compared with a centigrade thermometer, the

scales would be seen to be simply related (Fig. 155). If we designate absolute temperatures by A. and centigrade temperatures by C., then 373°A . is 100°C ., and 253°A . is -20°C . That is, absolute degrees are obtained by adding 273 *algebraically* to centigrade degrees.

How is absolute temperature used? Suppose we have 273 cc. of gas at 0°C . This volume becomes 274 cc. at 1°C . and 280 at 7°C . Now 0°C ., 1°C ., and 7°C . are 273°A .,

274° A., and 280° A., respectively. That is, stated in general terms as the **law of Charles**, we can say:—

At constant pressure the volumes of a given sample of gas at different temperatures vary directly as the absolute temperatures.

341. How we apply the law of Charles.—If we have 100 cc. of oxygen at 25° C. and wish to know what the volume would be at 0° C., we do not have to cool the gas to 0° C. and then measure the volume. We know: (1) that a gas contracts uniformly for each degree of fall in temperature, and (2) that the volumes vary directly as the absolute temperatures. Hence we can *compute* the volume to which the 100 cc. would contract if it were cooled from 25° to 0° C. The steps in the computation are these:—

(a) Change each centigrade temperature to absolute temperature by adding 273.

(b) Make a proportion involving the relation stated in (2), *i.e.*, observed volume: required volume :: observed absolute temperature: required absolute temperature.

(c) Solve the proportion for x .

Thus: (a) $25 + 273 = 298$, and $0 + 273 = 273$; (b) $100 : x :: 298 : 273$; (c) $x = 100 \times \frac{273}{298} = 91.6$. That is, 91.6 cc. is the volume 100 cc. would become if cooled from 25° C. to 0° C.

This form of computation is sometimes confusing. So a simpler one may be used, if desired. Since the temperature is lower, the volume will be smaller, because volumes change in the same way as the temperatures. Obviously, in the example given, 100 must be multiplied by a fraction having the numerator smaller than the denominator, *i.e.*, $100 \times \frac{273}{298} = 91.6$.

The mathematical process described in the above paragraphs is called **correcting for temperature**.

342. The relation between volume and pressure, and the law of Boyle.—Many gases are collected in bottles or tubes filled with water. In measuring the volume of the gas, the levels of the water are made the same inside and outside the collecting vessel by raising or lowering this vessel. When the levels are the same, the gas is under atmospheric pressure, *i.e.*, the pressure of the atmosphere exerted on the exposed

surface of the liquid is transmitted through the water to the gas. Hence the pressure which the gas is under when the volume is read is the pressure of the atmosphere.

The pressure of the atmosphere is found by reading the barometer. A common form of barometer is shown in Fig.



FIG. 156.—A barometer.

156. Near the top is a scale on which we can read the height of the mercury column. That is, by reading on the scale the height of the mercury — “reading the barometer” — we are measuring the pressure of the atmosphere at the time of the observation. The normal height of the barometer is 760 millimeters (mm.). The pressure of the atmosphere when the barometer is 760 mm. is called **normal or standard pressure**. It is also called **one atmosphere**.

The effect of pressure on the volume of a gas was first studied by the English chemist Boyle. He found that the volume is halved when the pressure is doubled, and so on. That is, the volume and pressure are in an *inverse* relation. The general fact may be stated as the **law of Boyle**, thus:—

The volume of a gas at constant temperature changes inversely with changes in pressure.

343. How we apply the law of Boyle.— In most experiments in chemistry we actually read a gas volume at the prevailing pressure, but we usually want to know what the volume would be if the pressure were 760 mm. Since we know that volumes are inversely related to their corresponding pressures (§ 342), we can compute the volume a gas would have, if the pressure were changed to 760 mm. The steps in the computation are these:—

(a) Make a proportion involving the inverse relations of volumes and pressures, *i.e.*, observed volume : required volume :: required pressure : observed pressure.

(b) Solve the proportion for x .

For example, suppose we wish to know what volume 100 cc. at 775 mm. would have at 760 mm. (a) $100 : x :: 760 : 775$; (b) $x = 100 \times \frac{775}{760} = 102$. This result means that 102 cc. is the volume 100 cc. would become if the pressure were changed from 775 mm. to 760 mm.

If the above form of computation is confusing, a simpler one may be used. Since pressure and volume are inversely related, the less the pressure the larger the volume. So the observed volume must be multiplied by a fraction having the numerator larger than the denominator, *i.e.*, $100 \times \frac{775}{760} = 102$ cc.

The mathematical process described in the above paragraphs is called **correcting for pressure**.

344. How we correct a gas volume for both temperature and pressure. — Measuring gases usually involves both temperature and pressure. Hence we compute what the volume would be at 0° C. and 760 mm. by combining the two mathematical processes into a single calculation. This combined mathematical process is called **reducing to standard conditions**, and the final volume is called the **corrected volume**. Suppose the observed volume is 100 cc., the temperature 25° C., and the pressure 775 mm. Then the volume at standard conditions is computed thus: —

$$100 \times \frac{273}{298} \times \frac{775}{760} = 93.4$$

Sometimes the reduction to standard conditions is more conveniently performed by substituting the observed values in the corresponding mathematical formula: —

$$V_2 = \frac{V_1 \times P_1}{760(1 + (0.00366 \times t))}$$

In this formula, which merely involves the mathematical processes just described, V_2 = final volume, V_1 = observed volume, P_1 = observed pressure, t = observed temperature (centigrade), and $0.00366 = \frac{1}{273}$.

345. Finding the weight of a given volume of a gas. — The weight of one liter of oxygen is 1.429 gm. The weight of one liter of oxygen is readily found by experiment.

(a) The apparatus is shown in Fig. 157. A mixture of potassium chlorate and manganese dioxide is put in the test tube *A*. The part *AF* is weighed. The bottle *B* is filled with water. The empty bottle

D is weighed. The mixture is heated and oxygen forces water from *B* into *D*. When sufficient gas (about half the volume of *B*) has been

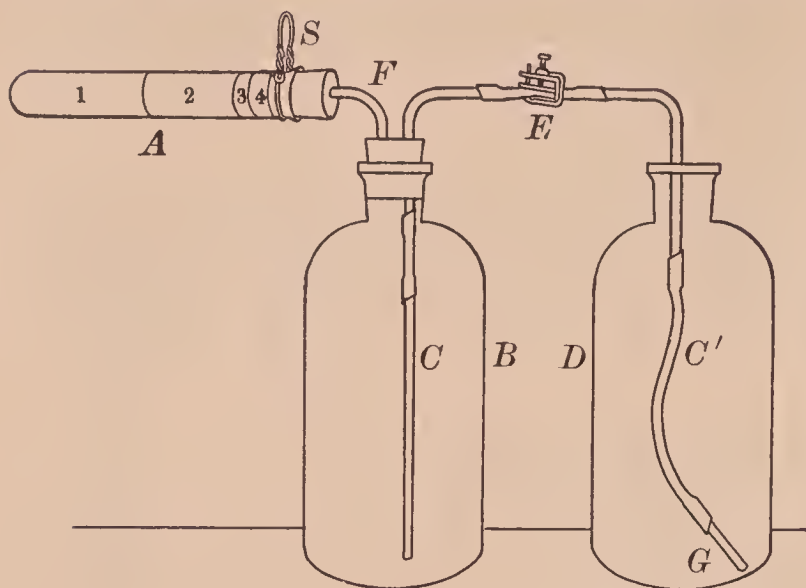


FIG. 157. — Apparatus for finding the weight of a liter of oxygen.

liberated, the heating is stopped and the apparatus is allowed to cool. (b) The temperature and pressure are read, say 20° C. and 755 mm. The levels in *B* and *D* are made the same (by raising one bottle) — to put the gas under atmospheric pressure. The water in *D* is measured; its volume is the same as the *volume of the oxygen*, say 1.75 liters. *AF* is weighed;

its loss is the weight of the oxygen, say 2.322 gm. (c) The observed volume is reduced to standard conditions; thus: $1.75 \times \frac{273}{293} \times \frac{760}{755} = 1.625$. (d) The weight of one liter of oxygen at 0° C. and 760 mm. is found by dividing the weight of the oxygen by its corrected volume; thus, $2.322 \div 1.625 = 1.429$.

We shall see later (§ 348, last paragraph) that allowance for the pressure of water vapor must be made in the numerical value of the final pressure when a gas is collected over water.

EXERCISES

1. State Charles's law. Illustrate it.
2. State Boyle's law. Illustrate it.
3. Give examples from everyday life of (a) expansion and of (b) contraction of gases caused by change of temperature.
4. Apply Exercise 3 to change of pressure.
5. (a) Change these centigrade readings to absolute: 100, 0, 15, - 15, 250, 273, - 273. (b) Change these absolute readings to centigrade: 273, 0, 200, 100, 473, 180, 373.

PROBLEMS

1. Reduce the following to the volume occupied at 760 mm.: (a) 20 cc. at 745 mm.; (b) 45 cc. at 765 mm.; (c) 450 cc. at 755 mm.; (d) 1.5 l. at 763 mm.
2. Reduce the following to the volume occupied at 0° C.: (a) 170 cc. at 80° C.; (b) 450 cc. at 15° C.; (c) 70.6 cc. at 17° C.; (d) 49 cc. at 19° C.

3. Reduce the following to the volume at standard conditions:
(a) 250 cc. at 780 mm. and 20° C.; (b) 140 cc. at 745 mm. and 21° C.
4. Reduce the following to the volume at standard conditions:
(a) 247 cc. at 720 mm. and 14° C.; (b) 1000 cc. at 750 mm. and 18° C.

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

Exercise 41 — Weight of 22.4 Liters of Oxygen.

TOPIC VII: LAWS AND THEORIES — KINETIC-MOLECULAR THEORY

346. Chemical laws and theories. — Many related facts are often summarized in a concise statement called a **law**. The explanation of a group of related facts is called a **theory**.

347. The kinetic-molecular theory of the structure of gases. — Gases behave alike in many ways. (1) They **expand** indefinitely and fill the whole containing vessel. This tendency is shown by the pressure exerted on the inside walls of the vessel or by the rapid escape through a hole, *e.g.*, a puncture in an automobile tire. (2) They **diffuse** readily, *i.e.*, they mix quickly and uniformly, and likewise pass through porous substances. Thus, ammonia is quickly detected in a room when a bottle of this substance is opened. (3) They are **highly compressible**, *e.g.*, a large volume of air can be pumped into an automobile tire; recall also that a large volume of oxygen, hydrogen, and carbon dioxide can be forced into small metal cylinders. (4) Gases **change uniformly in volume with changes in temperature and in pressure**.

The uniform behavior of gases led to a theory of their structure called the **kinetic-molecular theory**. The essentials of this theory are as follows: —

(1) A gas is made up of a large number of exceedingly minute particles called **molecules**. The molecules of a given gas are alike.

(2) The molecules of a gas are **relatively far apart**, *i.e.*, the distances between molecules are large compared with the

molecules. They are exceedingly small particles scattered throughout a very large space.

(3) The molecules of a gas are **moving rapidly** in all directions, striking each other and the walls of the containing vessel. Being **elastic**, they rebound and continue to move ceaselessly without loss of velocity. These blows, or **impacts**, **produce pressure**, and the series of rapid blows produces the effect of uniform and constant pressure.

(4) The movements of the molecules of a gas increase in velocity as temperature rises, and decrease as it falls. A definite **change in temperature changes the average velocity** of the molecules, thereby producing a definite change in volume (if the pressure is kept constant).

(5) The molecules have **little or no tendency to cohere**, *i.e.*, they lead an independent existence, being far apart relatively, except at great concentration.

Let us interpret the behavior of gases by the kinetic-molecular theory.

Consider the **law of Boyle**. When a gas is compressed, the molecules are pressed more closely together. And when a gas is compressed to half its volume, the pressure produced by the blows of the moving molecules is doubled because the number of blows per second against the walls is doubled.

Consider the **law of Charles**. The molecules move more rapidly, and consequently require more space when the temperature is raised; and the change in the average velocity of the molecules is proportional to the change in temperature, *i.e.*, the expansion (or contraction) is uniform with the temperature.

Again, the rapid movement of gases called **diffusion** is adequately interpreted by the constant motion of the molecules.

Finally **liquefaction**, which occurs when a gas is reduced to a low temperature and subjected to great pressure (§ 158), is explained as follows: the lowering of temperature slows up the velocity of the molecules and the increasing of pressure forces them nearer together, so that their fundamental tendency to cohere slightly becomes greater and manifests itself in the formation of larger particles (than molecules) which eventually become a mass of liquid.

TOPIC VIII: VAPOR PRESSURE — VOLUMETRIC COM-
POSITION OF WATER — GAY-LUSSAC'S LAW OF
GAS VOLUMES — HYDROGEN PEROXIDE

348. Vapor pressure. — Evaporation produces pressure, which is called the vapor pressure of water, or merely **vapor pressure**.

The fact that evaporation produces pressure can be shown by a simple experiment.

The dry bottle (Fig. 158, left) is fitted with an open U-shaped tube partly filled with a colored liquid (*e.g.*, dilute ink) to serve as an indicator of pressure. When the stopper is removed, a little water poured into the bottle, and the stopper quickly replaced, the water begins to evaporate. As the water evaporates, the colored liquid shows an increase in pressure (Fig. 158, right).

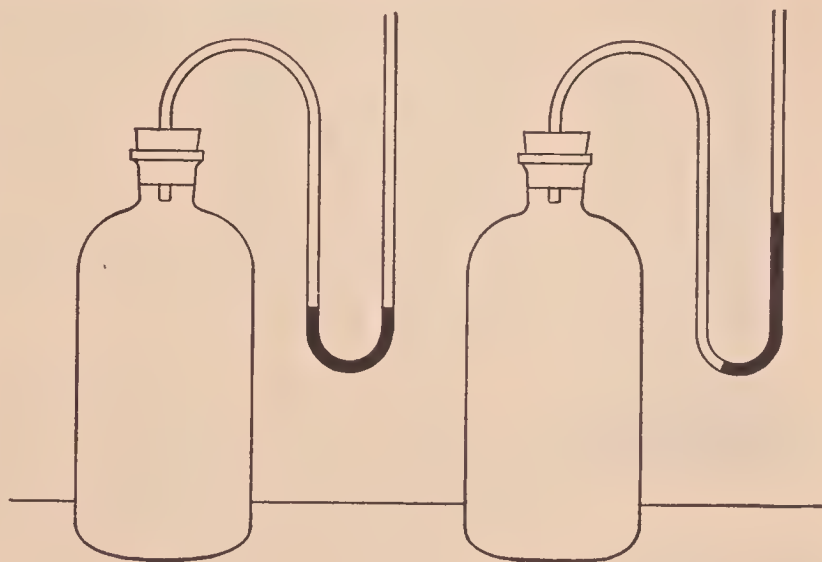


FIG. 158. — Experiment to illustrate vapor pressure. In the dry bottle (on the left) the colored liquid in the bent tube shows no pressure. Whereas, after water has been added, the colored liquid shows pressure in the bottle (on the right).

The amount of pressure exerted by water vapor depends solely on the temperature

— not on the quantity of water. This is readily seen by comparing the heights of the mercury in the fine-bore tubes shown in Fig. 159.

Each tube was first filled with mercury and inverted in the dish of mercury. In each tube the mercury sank to the same point (760 mm.). In tube *A* there is no water vapor in the space above the mercury, and the height of the mercury column is 760 mm. A drop of water was forced up into the tubes *B* and *C* by means of a medicine dropper. In *B* the space above the mercury is filled with water vapor kept at 20° C.; the vapor exerts a pressure and forces the mercury down to nearly 742 mm. That is, water vapor at 20° C. exerts a pressure equal to 18 mm. of

mercury. Similarly, in *C* the space is filled with water vapor kept at 50° C., and the mercury is forced down to 668 mm., the water vapor at this temperature exerting a pressure of 92 mm.

Vapor pressure and boiling point are related. The vapor escaping from water boiling in an open vessel overcomes the pressure of the atmosphere upon the surface of the water. Since the normal pressure of the atmosphere is 760 mm., the normal boiling point, so to speak, is 100° C. The boiling

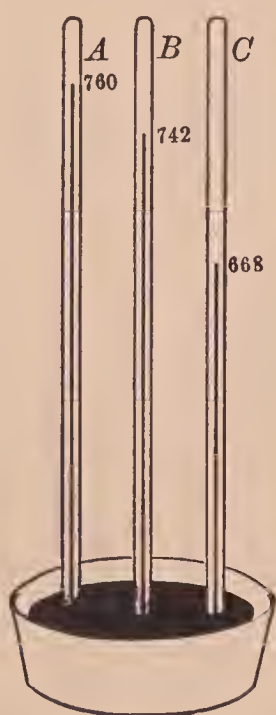


FIG. 159. — Experiment to show that the amount of vapor pressure depends on the temperature.

point becomes lower as the pressure is decreased and higher as the pressure is increased. Warm water will boil under the receiver of an air pump and on the top of a high mountain, because under these conditions the pressure is less than normal. In a pressure cooker the temperature of the water is above 100° C. On the other hand in a vacuum vessel, such as is used to evaporate sugar solutions, the boiling point is often as low as 70° C.

The pressure exerted by water vapor has a definite value for each temperature. These values can be found in the Table of Vapor Pressure given in the APPENDIX.

A practical application of vapor pressure is often made in computing the weight of a gas measured over water. Thus, in finding the weight of a liter of oxygen (§ 345) the gas is allowed to stand over the water long enough to become saturated with water vapor, that is, the bottle finally contains a mixture of oxygen and the maximum amount of water vapor at the given temperature. In such a mixture, each gas (oxygen and water vapor) shares the total atmospheric pressure. Hence the actual pressure exerted by the oxygen is found by subtracting the pressure of the water vapor (*a* in the table of vapor pressure) from the total pressure (read on the barometer). The corrected pressure is used in the formula for reducing the volume of a gas to its volume at 0° C. and 760 mm. (§ 345, next to last paragraph). Thus, if the temperature is 20° C., the vapor pressure as found in the table is 17.4. The formula then becomes —

$$1.75 \times \frac{273}{293} \times \frac{(755 - 17.4)}{760} = x$$

349. Efflorescence and vapor pressure. — The water vapor escaping, however slowly, by the efflorescence of a hydrate (crumbling of a crystallized salt due to loss of water of hydration, § 86), exerts a slight vapor pressure. If this vapor pressure is greater than the pressure of the water vapor in the atmosphere, the substance will lose water of hydration. That is, the substance will effloresce. Some hydrates do not effloresce at all, or only slightly, because their vapor pressure is less than the average vapor pressure of the air. Crystallized barium chloride ($\text{BaCl}_2 \cdot 2 \text{H}_2\text{O}$) and gypsum (selenite — $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$) belong to the latter class.

350. Deliquescence and vapor pressure. — Water vapor from the air condenses on the surface of soluble solids and produces a very concentrated solution. Such a solution has a much lower vapor pressure than the average pressure of the water vapor in the air. The solution, therefore, continues to take up water until its vapor pressure equals the pressure of the water vapor in the air.

351. Volumetric composition of water. — The volumetric composition of water is determined by measuring the volumes of hydrogen and oxygen that combine to form water.

A sketch of one form of apparatus is shown in Fig. 160. The essential part is the eudiometer *A*. It is a graduated glass tube closed at the upper end. Near this end two platinum wires are fused into the glass. The outer ends are looped and the inner ends are near together so that an electric spark will leap across the gap and produce enough heat to cause the two gases to unite.

The eudiometer is filled with mercury and inverted in the jar of the same liquid. Hydrogen is introduced until the eudiometer is about one fourth full. The mercury levels inside and outside are made the same, and the volume of hydrogen is read accurately. The temperature and pressure are also read. Approximately an equal volume of oxygen is then introduced, the levels are adjusted, and the total volume read accurately. Each volume is corrected for temperature and pressure (§ 344). The difference between the two corrected volumes is the volume of oxygen. An excess of oxygen is needed to lessen the violence of the explosion; this excess takes no part in the chemical change.

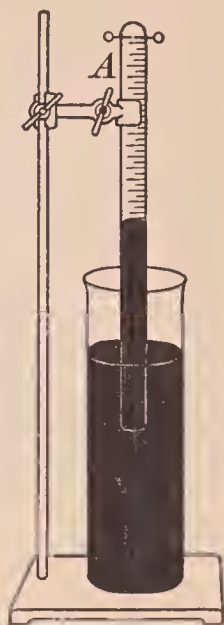


FIG. 160. — Apparatus for determining the volumetric composition of water.

The combination of the two gases is caused by connecting the looped ends of the platinum wires with an induction coil and battery, and passing a spark across the gap. A slight explosion indicates combination. The mercury, after the shock from the explosion, rises and nearly fills the

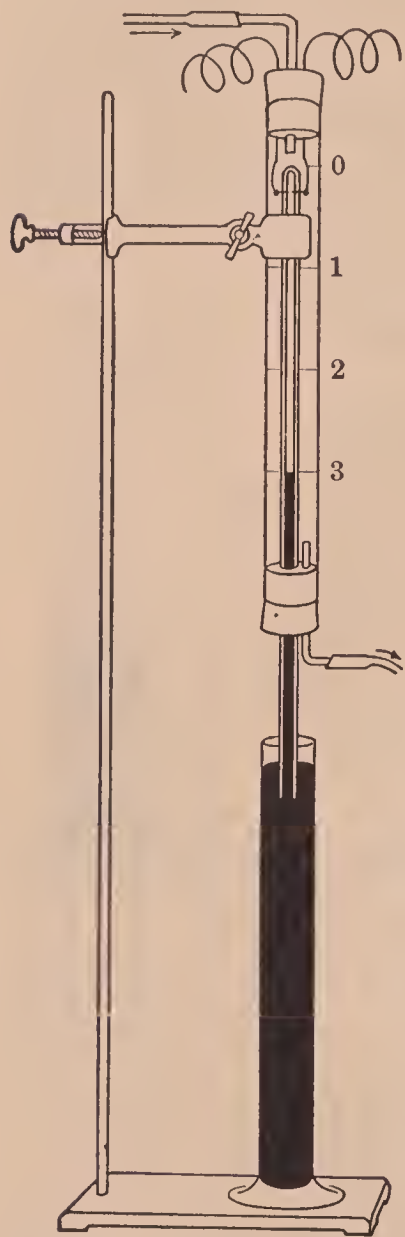


FIG. 161. — Apparatus for showing that 2 volumes of water vapor are formed by exploding 2 volumes of hydrogen and 1 volume of oxygen.

formed — provided all the gases are measured at the same pressure and the same temperatures (about 100°C). This result means that the volumes of the three gases — hydrogen, oxygen, and steam — involved in this reaction are expressed by 2, 1, and 2, *i.e.*, by small whole numbers.

eudiometer. The volume of the water produced is too minute to measure in this apparatus. After the mercury and residual gas (oxygen) are cool, the levels are adjusted, and the volume of gas is read (as well as the temperature and pressure). The corrected volume of this gas is subtracted from the corrected volume of oxygen, thus giving the actual volume of oxygen that combined with all the hydrogen to form water.

An example will make this experiment clear. Suppose the corrected volumes were: —

Volume of hydrogen added	22.3 cc.
Volume of hydrogen and oxygen added	41.5 cc.
Volume of oxygen added	19.2 cc.
Volume of oxygen left	8.0 cc.

This means that $19.2 - 8$, or 11.2, cc. of oxygen were actually used. In other words the two gases combined in the ratio of 22.3 to 11.2, or very nearly 2 volumes of hydrogen to 1 volume of oxygen.

352. Gay-Lussac's law of gas volumes. — A modification of the experiment described in § 351 shows that 2 volumes of water vapor are formed when 2 volumes of hydrogen and 1 volume of oxygen unite.

In the apparatus (Fig. 161) the eudiometer is surrounded by a large tube through which steam is passed, thereby preventing the condensation of the water vapor. If 2 volumes of hydrogen and 1 volume of oxygen are exploded, 2 volumes of water vapor are

When other chemical changes involving gases are studied, simple numerical relations are also found. This general fact, which was discovered by the French chemist Gay-Lussac (Fig. 162), in 1808, may be stated as a law, thus: —

In a chemical change the volumes of the gases can be expressed by small whole numbers.

This law will be used in a later topic (§ 363).

EXERCISES

1. Describe the experiment which shows (a) evaporation produces vapor pressure and (b) the amount of vapor pressure depends on temperature.

2. What is the vapor pressure of water at $20^{\circ}\text{C}.$? At $100^{\circ}\text{C}.$?

3. Interpret (a) efflorescence and (b) deliquescence by the principle of vapor pressure.

4. State the volumetric composition of water. How is it found?

5. State and illustrate Gay-Lussac's law.

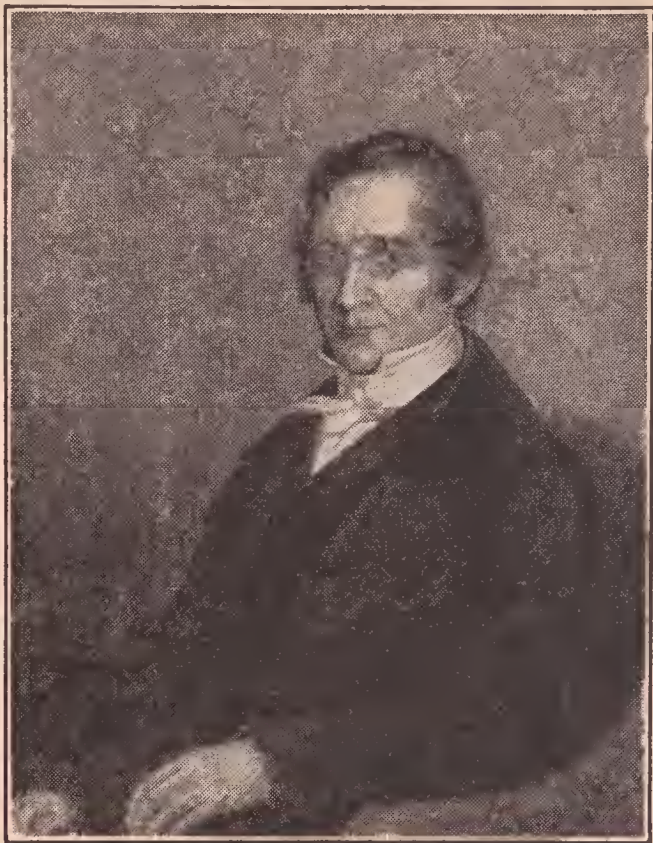


FIG. 162. — The French chemist Gay-Lussac (1787–1850), who first studied the simple relation of gas volumes in chemical changes.

PROBLEMS

1. What would be the volume of the *dry* gas at $0^{\circ}\text{C}.$ and 760 mm.? (a) 80 cc. at 750 mm. and $17^{\circ}\text{C}.$; (b) 100 cc. at 765 mm. and $19.5^{\circ}\text{C}.$

2. A mixture of 500 cc. of oxygen and 1250 cc. of hydrogen — both at the normal temperature and pressure — is exploded. What volume, if any, of gas will remain? How much? Which gas?

353. Hydrogen peroxide. — This is a compound of hydrogen and oxygen, which decomposes readily into oxygen and water. The commercial solution (3 per cent) is used to bleach hair, etc., and to sterilize wounds.

TOPIC IX: LAWS OF THE CONSERVATION OF MATTER
AND DEFINITE PROPORTIONS — ATOMIC THEORY —
ATOMS AND MOLECULES — ATOMIC WEIGHTS

354. Law of the conservation of matter. — The terms *law* and *theory* are defined in § 346.

In a chemical change the total weight of the matter involved is not altered. That is, the sum of the weights of the original substances equals the sum of the weights of the final substances. This general fact about chemical change is summed up by the **law of the conservation of matter**, thus:—

No weight is lost or gained in a chemical change.

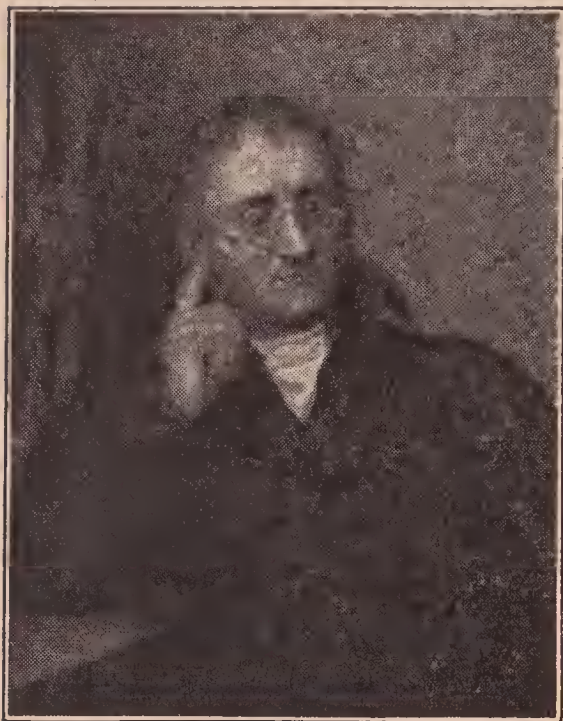


FIG. 163. — The English chemist Dalton (1766–1844), who proposed the atomic theory.

355. Law of constant composition. — In all chemical compounds the different constituents are present in a definite and constant proportion by weight. This general fact, stated in the form of a law, becomes the **law of constant composition** or the **law of definite proportions**, thus:—

A given chemical compound always contains the same elements in the same proportion by weight.

356. The atomic theory. — The theory that interprets the facts summarized in the two fundamental laws just stated is called the **atomic theory**. It was proposed about 1803 by the English chemist Dalton (Fig. 163). The essential points in Dalton's atomic theory are:—

(1) Elements are made up of very small particles called atoms.

(2) Atoms of the same element are alike and have an unvarying weight, called the atomic weight.

(3) Atoms of different elements differ from one another in weight.

(4) In a chemical change undivided atoms unite, are separated, or exchange places in the ratio of their particular weights.

The atomic theory means in a few words that matter is composed of atoms, which remain undivided in chemical changes.

With the help of the atomic theory, many facts about elements, compounds, and chemical change can be made much clearer (§§ 358, 359).

357. Atoms and molecules. — An **atom** is the smallest, indivisible particle of an element. It is the smallest part of an element which participates in a chemical change.

A **molecule** is a chemical combination of two or more atoms. If the atoms are alike, the molecule is a molecule of an element, *e.g.*, a molecule of oxygen consists of two atoms of the element oxygen (O_2). If the atoms are not alike, the molecule is a molecule of a compound, *e.g.*, a molecule of water consists of two atoms of hydrogen and one of oxygen (H_2O). A molecule is the smallest particle of a compound. Thus, a molecule of water is the smallest particle of the compound water, because if we try to produce a smaller particle, we obtain atoms of the elements hydrogen and oxygen.

According to present views an **atom** is essentially electrical. It consists of a **nucleus** surrounded by **electrons** moving in orbits. The nucleus is positively charged. Each electron is negatively charged. The positive charge on the nucleus is electrically balanced by the total negative charges on the surrounding electrons. Hence an atom as a whole is electrically neutral. A **molecule** is a group of atoms held together electrically. (Refer to §§ 358, 424, 529.)

358. Interpretation of chemical change by the atomic theory. — (1) A sample of the element copper consists of many millions of atoms of copper. A sample of oxygen likewise consists of atoms of oxygen. When the chemical change occurs between copper and oxygen, atoms of copper combine with atoms of oxygen and form molecules of the compound copper oxide. And this combining of atoms into

molecules continues until all the atoms of copper or all the atoms of oxygen (or under certain conditions all the atoms of both elements) are used up.

(2) Similarly, the decomposition of mercuric oxide is the separation of numberless molecules of the compound mercuric oxide into atoms of the elements mercury and oxygen.

(3) So also, the liberation of hydrogen from sulfuric acid is the exchange of atoms of zinc for the atoms of hydrogen in the compound sulfuric acid.

Chemical change can also be interpreted by the electron theory. Atoms lose or gain electrons more or less readily. Thus, copper atoms tend to lose electrons and oxygen atoms to gain them. When atoms of copper and of oxygen form molecules of copper oxide, each copper atom loses two electrons which are gained by an oxygen atom. The copper atoms thereby become positive and the oxygen atoms negative. And each pair of oppositely charged atoms is held together electrically as a molecule of copper oxide.

359. How the atomic theory helps us explain the two fundamental laws of chemical change. — (1) The law of the conservation of matter states that there is no loss or gain of weight in a chemical change. According to the atomic theory the weight of an atom is never changed. This means that in the case of copper and oxygen, no atoms are created or destroyed. Hence the weight of the copper oxide formed must equal the sum of the weights of the copper and oxygen used up chemically. Inasmuch as in all chemical changes there is no loss or gain in weight, it is obvious that the atomic theory, which assumes unvarying weights of atoms, is in accord with the law of the conservation of matter.

(2) The law of constant composition states that a given compound always consists of the same elements in a fixed proportion. According to the atomic theory, molecules are formed by the union of a definite number of whole atoms of each element. Each molecule of the compound copper oxide, for example, would consist of one or more atoms of copper united with one or more atoms of oxygen. Therefore the composition of each molecule of copper oxide would be constant, *i.e.*, each molecule would consist of the same ele-

ments united in a constant proportion by weight. This means that the composition of copper oxide would always be a certain per cent of copper and a certain per cent of oxygen. Since all chemical compounds have been found to have a constant composition, the atomic theory is in harmony with the law of constant composition.

360. Atomic weights. — According to the atomic theory atoms of the same element always have the same weight but atoms of different elements have different weights. This means, for example, (1) that an atom of oxygen throughout all its varied changes retains its weight, and (2) that this weight differs from the weight of other kinds of atoms. The weights of different kinds of atoms are called the **atomic weights** of the elements, or briefly atomic weights. These weights have been determined by very accurate experiments (§ 377). A table giving the exact, as well as the approximate, values can be found on the inside of the back cover of this book. **The standard atomic weight is oxygen = 16.**

Atomic weights are relative weights. That is, the atomic weight of copper is 63.57, not 63.57 gm. or any other actual weight, but 63.57 as long as 16 is accepted as the standard atomic weight of oxygen.

The exact determination of atomic weights is a difficult task. Until this subject is discussed (§§ 375–378), it will be well enough to use the approximate weights from the table as needed.

EXERCISES

1. Define law and theory as used in science.
2. State the law of conservation of matter. Illustrate it by the decomposition of mercuric oxide.
3. State the law of constant composition. Illustrate it by the gravimetric composition of water.
4. State the four points in the atomic theory.
5. (a) What is an atom? A molecule? (b) Discuss the relation of atoms to molecules.
6. Describe a chemical change by the (a) atomic and (b) electron theory.
7. Interpret by the atomic theory the two laws: (a) conservation of matter, and (b) constant composition.
8. What are atomic weights?

9. Learn the approximate atomic weight of these elements: Hydrogen, oxygen, nitrogen, carbon, copper, iron, sulfur, chlorine.

10. As in Exercise 9: Sodium, calcium, lead, magnesium, mercury, silver, zinc.

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

Exercise 22 — Formation of the Compound Copper Sulfide.

TOPIC X: EQUIVALENT WEIGHTS

361. Equivalent weights. — The **equivalent weight** of an element is the weight that combines with or replaces 8 grams of oxygen. For example, 12 grams of magnesium combines with 8 grams of oxygen. Therefore 12 is the equivalent weight of magnesium. Similarly, hydrogen and oxygen combine in the ratio of 1 to 8; therefore 1 is the equivalent weight of hydrogen.

Equivalent weights are sometimes called **reacting weights**, or simply **equivalents**. The term *equivalent weights* is preferable, because they actually are the weights chemically equivalent to each other. Thus, 1 gm. of hydrogen combines with 35.5 gm. of chlorine, and this 1 gm. of hydrogen can be replaced chemically by 32.5 gm. of zinc, 12 gm. of magnesium, 9 gm. of aluminum, or 20 gm. of calcium, and so on. These elements are chemically equivalent in the ratio of these weights.

In the laboratory the equivalent weights of certain elements can not be determined directly in terms of oxygen. They are determined by finding the weight that combines with or replaces the equivalent weight of some other element, usually hydrogen. Thus, 32.5 grams of zinc replace 1 gram of hydrogen from hydrochloric acid; therefore 32.5 is the equivalent weight of zinc.

Comparison of the equivalent weight with the (approximate) atomic weight of the same element reveals an important relation, as may be seen by Table XI. An examination of this comparative table shows an integral relation between equivalent weights and atomic weights. In other words,

TABLE XI. — COMPARISON OF EQUIVALENT WEIGHTS
AND ATOMIC WEIGHTS

ELEMENT	EQUIVALENT WEIGHT	ATOMIC WEIGHT	MULTIPLE
Oxygen	8	16	2
Aluminum	9	27	3
Bromine	80	80	1
Calcium	20	40	2
Carbon	3	12	4
Chlorine	35.5	35.5	1
Hydrogen	1	1	1
Magnesium	12	24	2
Silver	108	108	1
Sodium	23	23	1
Sulfur	16	32	2
Zinc	32.5	65	2

the atomic weight of an element is identical with its equivalent weight or is a simple integral multiple of it. These integral multiples are the same as the numerical valence of the element (§ 117).

362. The difference between equivalent and atomic weights. — The equivalent weight of an element, as previously stated, is the weight that combines with or displaces 8 gm. of oxygen. That is, equivalent weights are merely weights in a scheme which is based on $O = 8$. But 8 is not the unit used in chemistry to express the composition of compounds or the quantitative relations of the elements. The quantitative unit is 16. Equivalent weights are empirical. Whereas atomic weights are part of the whole structure of theoretical chemistry which is erected on all the facts, laws, and theories of chemistry.

EXERCISES

1. Define and illustrate equivalent weight.
2. What is the equivalent weight of oxygen, hydrogen, zinc, magnesium, aluminum, sodium, calcium, chlorine, silver?
3. What is the difference between an equivalent weight and an atomic weight?

PROBLEMS

1. Calculate the equivalent weights of the respective metals from the following data: (a) 0.5 gm. of calcium unites with 0.2 gm. of oxygen to form calcium oxide (CaO). (b) 15 gm. of mercury unite with 1.2 gm. of oxygen to form mercuric oxide (HgO).

2. Calculate the equivalent weight of sodium from the following: (a) 2.3 gm. of sodium liberate 0.1 gm. of hydrogen from water. (b) 1.15 gm. of sodium liberate 555.5 cc. of hydrogen (at standard conditions).

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

Exercise *21 — Equivalent Weight of Zinc.

Exercise 20 — Equivalent Weight of Magnesium.

Exercise S18 — Equivalent Weight of Aluminum.

TOPIC XI: GAY-LUSSAC'S LAW — AVOGADRO'S LAW — MOLECULAR WEIGHTS — MOLECULES — FORMULAS — MOLECULAR EQUATIONS

363. Gay-Lussac's law of gas volumes. — This law was discussed in § 352.

The volumes of gases involved in several chemical changes are shown in Table XII.

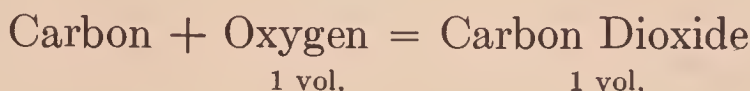
TABLE XII. — COMBINATION OF GASES BY VOLUME

VOLUMES OF COMBINING GASES	VOLUMES OF GASEOUS PRODUCT
2 volumes of hydrogen 1 volume of oxygen	2 volumes of water vapor
1 volume of hydrogen 1 volume of chlorine	2 volumes of hydrogen chloride
1 volume of nitrogen 3 volumes of hydrogen	2 volumes of ammonia
1 volume of nitrogen 1 volume of oxygen	2 volumes of nitric oxide

It is clear from the above table that the volumes of the gases can be expressed by small whole numbers. This simple relation is true of all gas reactions, and may be stated as **Gay-Lussac's law**, thus: —

In a chemical change the volumes of the gases can be expressed by small whole numbers.

This law applies only to gases. For example, carbon is not a gas, though it is frequently involved in reactions with gases, *e.g.*: —



So we omit carbon as far as volume is concerned, and say carbon unites with 1 volume of oxygen (O_2) to form 1 volume of carbon dioxide (CO_2).

364. Avogadro's law. — In 1811 the Italian physicist Avogadro proposed an explanation of the simple numerical relation of gas volumes in a chemical change. It is usually called **Avogadro's law** and may be stated thus: —

Equal volumes of gases under like conditions of temperature and pressure contain the same number of molecules.

This law means, for example, that a liter of oxygen contains just as many molecules as a liter of hydrogen, nitric oxide, or any other gas, if the temperature and pressure are the same. Hence, if equal volumes of gases are weighed, the weights are in the same ratio as the weights of single molecules of the gases.

365. How Avogadro's law is used to find molecular weights. — Let us consider carbon dioxide and oxygen. A liter of carbon dioxide weighs 1.98 gm. and a liter of oxygen 1.43 gm. at 0°C . and 760 mm. Therefore the weight of a liter of carbon dioxide is 1.38 times that of a liter of oxygen (*i.e.*, $1.98 \div 1.43 = 1.38$). Since a liter of each gas contains the same number of molecules, the weight of the carbon dioxide molecules is 1.38 times the weight of the oxygen molecules. This means that the molecular weight of carbon dioxide is 1.38 times the molecular weight of oxygen.

The molecular weight of oxygen is 32 (see next paragraph). Hence the molecular weight of carbon dioxide is 32 times

1.38 = 44. Therefore 44 is the molecular weight of carbon dioxide.

366. Why the molecular weight of oxygen is 32. — There are two reasons. (1) An atom of oxygen weighs 16, because this number has been adopted by chemists as the standard atomic weight (§ 378). (2) A molecule of oxygen contains 2 atoms, as will be shown in § 368. Hence the molecular weight of oxygen is 32 (*i.e.*, 2 times 16).

367. Finding molecular weights by the vapor density method. — The method of finding molecular weights described in § 365 is called the **vapor density method**. The steps are (1) find the vapor density (*i.e.*, relative weight) referred to oxygen, and (2) multiply this value by 32.

The expression "*vapor density referred to oxygen*" means the number found by dividing the weight of a given volume of a gas or vapor by the weight of an equal volume of oxygen (measured at the same temperature and pressure). Thus, in the example given above the number 1.38 is the vapor density of carbon dioxide (*i.e.*, $1.98 \div 1.43$).

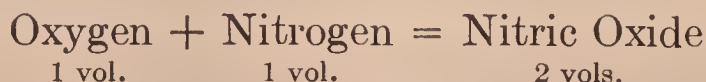
Therefore, in brief: —

Molecular Weight = Vapor Density referred to Oxygen times 32.

Some substances can not be vaporized without decomposition. The molecular weights of such substances can not, of course, be found by the vapor density method.

No experimental method has been devised for determining the molecular weight of a substance in the solid state (*i.e.*, not dissolved or vaporized); it is customary to assume that the molecular weight of such substances is the sum of the atomic weights in the simplest formula (§§ 104, 105).

368. A molecule of oxygen contains two atoms. — We use Gay-Lussac's and Avogadro's laws to prove that a molecule of oxygen contains two atoms. When oxygen and nitrogen combine to form nitric oxide, the volumes used and produced can be expressed (according to Gay-Lussac's law) thus: —



Now according to Avogadro's law, equal volumes of gases

contain the same number of molecules. Suppose there are 1000 molecules of oxygen in 1 volume. Then by Avogadro's law there are 2000 molecules of nitric oxide in 2 volumes of this gas. Now every molecule of nitric oxide must contain at least one atom of oxygen; and the 2000 molecules must contain at least 2000 atoms of oxygen. But these 2000 atoms of oxygen were provided by the 1000 molecules of oxygen. Therefore, each molecule of oxygen must contain at least 2 atoms of oxygen.

369. Molecules of other elementary gases contain two atoms. — There are good reasons for dropping the "at least" and saying a molecule of oxygen contains 2 atoms. Thus, there is no reaction in which a given volume of oxygen and other elementary gases, *e.g.*, nitrogen, hydrogen, and chlorine, provides material for more than two volumes of the gaseous product. This means there is no reaction in which a molecule of these gases is divided into more than two parts. And so we conclude that the molecule of these gases contains only two atoms. Hence we write their formulas O_2 , N_2 , H_2 , and Cl_2 . It is clear now why we used these formulas in preceding sections for molecules of the gases.

370. A mole. — A mole of a substance is the number of grams numerically equal to its molecular weight. It is sometimes called a gram-molecular weight. Thus, a mole of carbon dioxide is 44 grams because the molecular weight is the number 44. Similarly, a mole of oxygen is 32 grams, of carbon monoxide is 28 grams, and of nitric oxide is 30 grams.

The volume occupied by one mole of oxygen (at 0° C. and 760 mm.) is 22.4 liters. Suppose we construct a box holding 22.4 liters (Fig. 164), and fill it with oxygen (at 0° C. and 760 mm.), the gas will weigh 32 grams. This must be so, because one liter of oxygen weighs 1.43 grams, and the volume occupied by 32 grams of oxygen will be $32 \div 1.43$, or 22.4 liters (in round numbers). Similarly, the volume occupied by one mole of carbon monoxide is 22.4 l., *i.e.*, $28 \div 1.25 = 22.4$.

This volume (22.4 liters) is sometimes called the gram-molecular volume, since it is the volume of the gram-molec-

ular weight. It is also called a uni-molar volume, because it is the volume of *one* mole. So it is clear that 1 mole of a gas and 22.4 liters of the same gas are equal — one being the weight and the other the volume of the same mass of gas.



FIG. 164. — A box holding 1 mole or 22.4 liters of a gas (actual length of one edge is 28.2 cm.).

371. How molecular weight is calculated by the molar method. — Suppose we construct several cubical boxes each holding 22.4 liters (Fig. 165), weigh each box, fill each with a gas (at 0°C . and 760 mm.), and weigh again. In each case the weight of the several gases

is numerically equal to the molecular weight. If the gases are nitric oxide, carbon monoxide, hydrogen chloride, and ammonia, the numbers obtained are 30, 28, 36.5, and 17. And these numbers are the molecular weights respectively of these gases.

Hence to find the molecular weight of a gas by the molar method, calculate the weight of 22.4 liters of the gas. . It

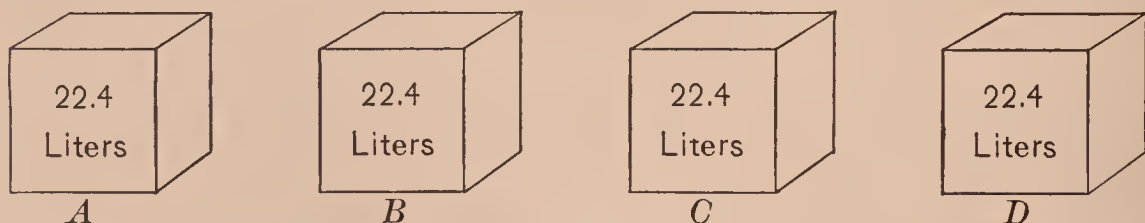


FIG. 165. — A mole of different gases occupies 22.4 liters. $A = 30\text{ gm. NO}$, $B = 28\text{ gm. CO}$, $C = 36.5\text{ gm. HCl}$, $D = 17\text{ gm. NH}_3$.

is not necessary to use such a large volume in the actual experiment. We simply find the weight of any convenient volume (from a table or by experiment) and then calculate the weight of 22.4 liters. Thus, if 1.5 liters of carbon monoxide (at 0°C . and 760 mm.) weigh 1.88 grams, the weight of 22.4 liters is found thus: $1.88 \div 1.5 = 1.25$; $1.25 \times 22.4 = 28$. Therefore 28 is the molecular weight of carbon monoxide.

372. Molecular formulas of compounds. — A formula of a compound represents by symbols the *kind and number* of atoms in a molecule.

In § 105 it was shown that the simplest formula of a compound can be calculated from the percentage composition by dividing the per cent of each element in the compound by the respective atomic weight, and then, if necessary, reducing the quotients to the smallest whole numbers. A formula thus calculated is called the **simplest formula** because it expresses in the simplest chemical way the proportions of the different elements in a compound. But it may not be its correct formula.

The **correct formula** of a compound must represent its molecular weight. That is, the sum of the weights represented by the kind and number of atoms in the correct formula must be equal (or very nearly equal) to the molecular weight found by experiment. Let us take an example. A compound was found by analysis to contain 92.3 per cent of carbon and 7.7 of hydrogen, and to have a vapor density of 2.4375. Dividing the percentages by the atomic weights, we have: $92.3 \div 12 = 7.7$, and $7.7 \div 1 = 7.7$. Since $7.7 : 7.7$ as $1 : 1$, the compound contains at least one atom each of carbon and hydrogen, and its simplest formula is CH. This formula corresponds to the molecular weight 13. But the vapor density 2.4375 requires the molecular weight 78 (*i.e.*, $2.4375 \text{ times } 32 = 78$), which is six times the weight (13) corresponding to the formula CH. Hence the molecular formula of this compound is not CH, but C_6H_6 .

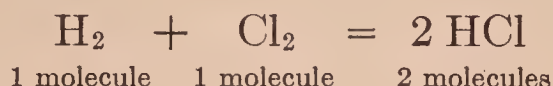
If the molecular weight of a compound can not be found by experiment, then the simplest formula is accepted as the molecular formula. For example, a certain compound contains 40 per cent of calcium, 12 of carbon, and 48 of oxygen. Dividing each per cent by the proper atomic weight, we have: $40 \div 40 = 1$, $12 \div 12 = 1$, $48 \div 16 = 3$. That is, one molecule of this compound contains (at least) 1 atom each of calcium and carbon, and 3 of oxygen; therefore the simplest formula is CaCO_3 . This is also accepted as its molecular formula, because the molecular weight can not be found by any known method.

373. Molecular formulas of elements. — Several gaseous elements have molecular weights which are twice the atomic weight. This means that the molecule consists of two atoms, and their molecular formulas are, for example, O_2 , H_2 , Cl_2 , N_2 (also Br_2). (Compare § 369.)

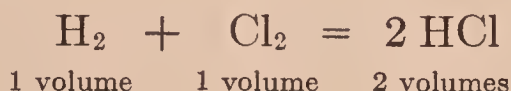
374. Molecular equations. — Reactions involving the common elementary gases should be expressed by molecular equations. Thus, the molecular equation for the formation of water vapor from hydrogen and oxygen is: —



This equation is read: Two molecules of hydrogen unite with one molecule of oxygen to form two molecules of water vapor. Since this equation correctly represents the interacting substances as molecules, the equation is correctly called a **molecular equation**. A molecular equation is sometimes called a **volumetric equation** or a **gas equation**, because it shows the volumes of gases involved in the reaction. Thus, the equation



may be written: —



because equal numbers of molecules represent equal volumes. The second equation is read: One volume of hydrogen and one volume of chlorine form two volumes of hydrogen chloride. It should be remembered that in molecular or volumetric equations a single molecule represents one volume of a gas (or vapor) and the coefficient indicates the number of volumes.

EXERCISES

1. State and illustrate (a) Gay-Lussac's law and (b) Avogadro's law.
2. (a) State the argument proving that a molecule of oxygen consists of two atoms. (b) Apply (a) to nitrogen.
3. Hydrogen and nitrogen combine in the ratio of 3 to 1 to form 2 volumes of ammonia. Show from this relation that a molecule of hydrogen contains at least two atoms.

4. What is the relation between molecular weight and vapor density?
5. Why is the formula of water vapor H_2O and not HO or H_2O_2 ?
6. How are the molecular weights of gases determined by (a) the vapor density method, and (b) the molar method?
7. Define and illustrate (a) molecular equation, (b) mole, (c) gram-molecular weight, (d) gram-molecular volume.
8. What is a molecular formula? What is the molecular formula of oxygen, nitrogen, chlorine, hydrogen?
9. How is a molecular formula determined? Illustrate.
10. Express the following as molecular equations: (a) One volume of phosphorus vapor and six volumes of chlorine form four volumes of phosphorus trichloride (PCl_3) vapor; (b) carbon and water (vapor) form hydrogen and carbon monoxide.

PROBLEMS

1. 1,000,000 molecules of hydrogen will unite with how many molecules of oxygen to form how many molecules of water vapor? What will be the relative weights of hydrogen and water vapor?
2. A liter of sulfurous oxide gas (SO_2) weighs 2.9 gm. Calculate the molecular weight of this compound. Compare with the theoretical molecular weight.
3. The vapor density of hydrogen chloride is 1.14. Calculate the molecular weight.
4. If 3000 cc. of an oxide of carbon weigh 3.75 gm., what is the molecular weight, formula, and name of the oxide?
5. Calculate the correct formula of the compound corresponding to (a) $\text{C} = 85.71$, $\text{H} = 14.29$, vapor density = 2.1875; (b) $\text{C} = 39.9$, $\text{H} = 6.7$, $\text{O} = 53.4$, vapor density = 1.906.
6. What volume of the constituent gases can be obtained by the complete decomposition of 6 l. of ammonia?
7. Write the equation for the reaction between nitric oxide (NO) and oxygen. What volume of oxygen is needed for 10 l. of nitric oxide? What will be the volume of the product?
8. The correct formula of a gas is CH_4 . (a) How many grams does a mole weigh? (b) What volume does this weight occupy? (c) What is the weight of 1 l. of the gas?
9. A gas contains 69.49 per cent of oxygen and 30.51 of nitrogen. (a) What is its simplest formula? (b) If 500 cc. weigh 2.042 gm., what is the correct formula?

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

Exercise 41 — Weight of 22.4 Liters of Oxygen.

TOPIC XII: FINDING ATOMIC WEIGHTS

375. Atomic weights.—According to Dalton's atomic theory (§ 356), atoms have the same weight if alike, but a different weight if different. And the relative weights of atoms are called **atomic weights**.

The standard for atomic weights is oxygen = 16.

376. Finding approximate atomic weights from molecular weights.—Approximate atomic weights can be determined from molecular weights.

The molecular weights of compounds can be determined by experiment (§§ 367, 371). After the molecular weights of several related compounds have been determined, we can readily find the approximate atomic weight of the constituent elements. That is, it is only necessary to apportion the molecular weights among the respective elements of the compounds, and then select the minimum weight in each case.

For example, let us apply this procedure to finding the atomic weight of carbon. The steps are as follows:

(1) Find by experiment the molecular weights of several compounds containing carbon.

(2) Find by analysis the per cent of carbon in each compound.

(3) Find the portion of carbon in each molecular weight by multiplying the molecular weight by the corresponding per cent of carbon.

(4) Select the minimum value as the approximate atomic weight.

The steps are embodied in Table XIII. In the table, column 1 contains the name of each compound, column 2 the corresponding molecular weight, column 3 the per cent of carbon in each compound, and column 4 the weight of carbon in the corresponding molecular weight. The weights in column 4 are found by multiplying the molecular weight (in column 2) of the compound by the corresponding per cent of carbon (in column 3); thus $28 \text{ times } 0.429 = 12$. The minimum value 12 is the atomic weight of carbon.

Obviously, the minimum weight must be the weight of a

TABLE XIII. — DETERMINATION OF THE ATOMIC WEIGHT OF CARBON

COMPOUND	MOL. WT.	PER CENT OF CAR- BON	WT. OF CAR- BON	COMPOUND	MOL. WT.	PER CENT OF CAR- BON	WT. OF CAR- BON
Carbon Monoxide	28	42.9	12	Ethylene.	28	85.7	24
Carbon Dioxide.	44	27.3	12	Acetylene	26	92.3	24
Methane . . .	16	75.0	12	Ether . .	74	64.9	48
Ethane. . . .	30	80.0	24	Propane .	44	81.8	36

single atom, for it is highly probable that one or more compounds in a representative group will contain only one atom of a given element; and the part of the molecular weight apportioned to this element will of course be its atomic weight. In the compounds that contain a multiple of this weight, it is likewise obvious that the molecule must contain several atoms of the element. Thus, the weight of carbon in ethane is twice that in methane, and we conclude that a molecule of ethane contains two atoms of carbon — a conclusion in harmony with other observations.

The numerical results obtained in applying the above method to the elements oxygen, hydrogen, chlorine, nitrogen, and carbon are summarized in Table XIV. In this table, for the sake of simplicity, whole numbers are

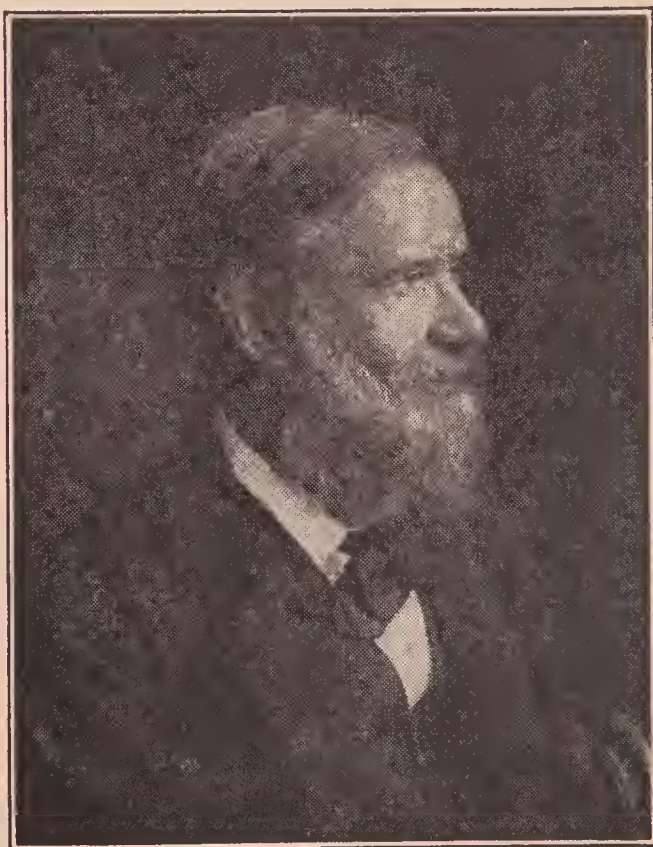


FIG. 166. — The Italian chemist Cannizzaro (1826–1910) whose work laid the foundations of our present system of atomic weights.

used (except in the case of chlorine) and per cents are omitted. The minimum weight in each case is the atomic weight of the element, *e.g.*, Cl = 35.5.

This method of determining approximate atomic weights was proposed about 1858 by the Italian chemist Cannizzaro (Fig. 166).

TABLE XIV. — DETERMINATION OF APPROXIMATE ATOMIC WEIGHTS

COMPOUND	MOLECULAR WT.	WT. OF OXY- GEN	WT. OF HYDRO- GEN	WT. OF CHLO- RINE	WT. OF NITRO- GEN	WT. OF CAR- BON
Water	18	16	2	—	—	—
Hydrogen Peroxide . . .	34	32	2	—	—	—
Hydrogen Chloride . . .	36.5	—	1	35.5	—	—
Ammonia	17	—	3	—	14	—
Nitric Acid	63	48	1	—	14	—
Nitrous Oxide	44	16	—	—	28	—
Nitric Oxide	30	16	—	—	14	—
Nitrogen Dioxide	46	32	—	—	14	—
Carbon Monoxide	28	16	—	—	—	12
Carbon Dioxide	44	32	—	—	—	12
Methane	16	—	4	—	—	12
Ethylene	28	—	4	—	—	24
Acetylene	26	—	2	—	—	24
Ether	74	16	10	—	—	48
Ethyl Alcohol	46	16	6	—	—	24
Chloroform	119.5	—	1	106.5	—	12
Carbon Tetrachloride . .	154	—	—	142	—	12
Cyanogen Chloride . . .	61.5	—	—	35.5	14	12
Minimum weight of each element		16	1	35.5	14	12

377. Exact atomic weights. — Atomic weights obtained from approximate molecular weights are, of course, approximate. When the approximate atomic weight of an element has been chosen by the method described in § 376, its exact atomic weight is determined by accurate chemical analysis of compounds prepared from carefully purified substances.

The general method can be illustrated by an actual case kindly furnished by the American chemist Richards (Fig. 167), who made exceptionally accurate determinations of atomic weights. In determining the atomic weight of chlorine he found that 28.26299 gm. of silver chloride were formed from 21.27143 gm. of silver. He accepted AgCl as the formula of silver chloride and 107.880 as the atomic weight of silver, and calculated the atomic weight of chlorine thus:—

$$28.26299 - 21.27143 = 6.99156$$

$$\begin{array}{ccccccc} \text{Wt. of silver} & : & \text{Wt. of chlorine} & :: & \text{At. wt. of silver} & : & \text{At. wt. of chlorine} \\ 21.27143 & : & 6.99156 & :: & 107.880 & : & x \end{array}$$

$$x = 35.458$$

378. International atomic weights.—An international committee formerly selected the most accurate atomic weight of each element (except oxygen, of course, which was adopted as 16 several years ago). These weights were embodied in a table published at frequent intervals and called the International Table of Atomic Weights. The table given on the inside of the back cover of this book is not an international table but a table of the most recent exact weights (together with other data) compiled by American chemists. In this table the accepted atomic weights are placed in one column and the corresponding approximate values (selected by the author) in another column. The approximate atomic weights in the table are sufficiently accurate for general use, *e.g.*, in making chemical calculations and in solving the problems in this book (unless otherwise directed).

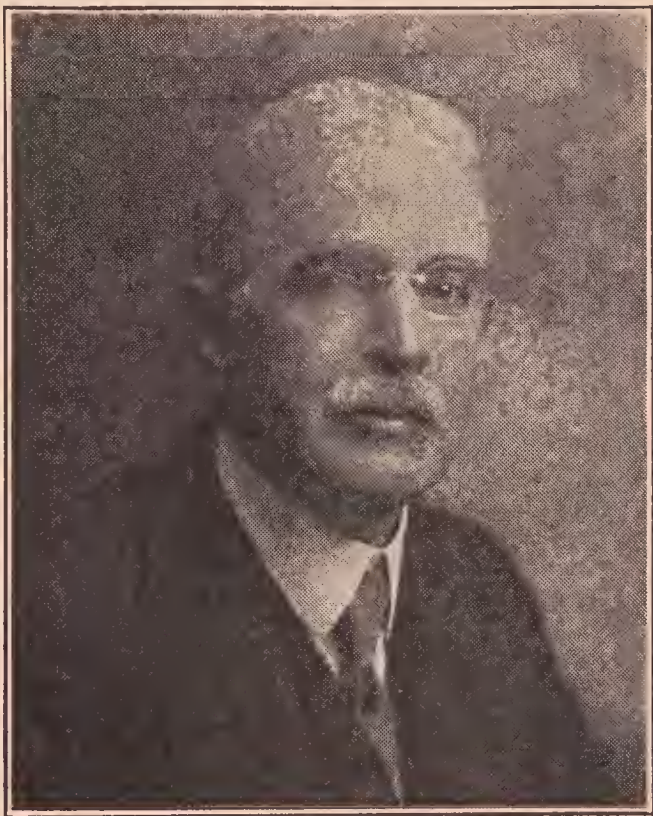


FIG. 167.—The American chemist Richards (1868–1928), who made exceptionally accurate determinations of atomic weights.

EXERCISES

1. State the four steps in finding atomic weights by the "minimum weight" method. Illustrate by carbon.
2. Why is 16 the atomic weight of oxygen?
3. What is the atomic weight of (a) Al, Ba, Br, Ca, C, Cl, Cu, F, Au, H; (b) I, Fe, Pb, Mg, Mn, Hg, N, O, P, K; (c) Si, Ag, Na, S, Sn, Zn?

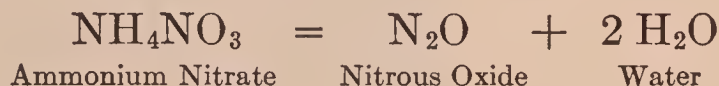
PROBLEMS

1. If 2 gm. of potassium chloride yield 3.84 gm. of silver chloride, calculate the exact atomic weight of potassium (assume Cl = 35.457).
2. In a synthesis of hydrogen bromide, 0.8606 gm. of hydrogen combined with 68.25033 gm. of bromine. Calculate the exact atomic weight of bromine (assume H = 1.008).

TOPIC XIII: NITROGEN OXIDES

379. Nitrogen oxides. — The three important nitrogen oxides are nitrous oxide (N_2O), nitric oxide (NO), and nitrogen dioxide (NO_2). There is also an oxide called nitrogen tetroxide (N_2O_4).

380. Nitrous oxide. — This gas is prepared by gently heating ammonium nitrate. The equation is: —



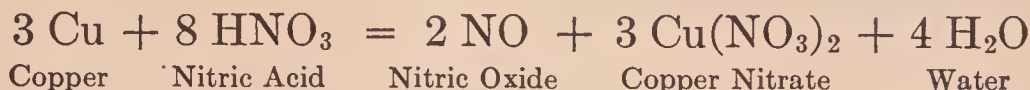
The gas is colorless, and has a faint but pleasant odor. It is soluble in water, and the solution has a sweet taste.

Nitrous oxide does not burn, but it supports the combustion of many well-burning substances, though not so vigorously as oxygen does. Thus, sulfur, if burning well, will burn in nitrous oxide. In its power to support combustion it resembles oxygen (§ 27). It is distinguished from oxygen by its failure to form brown fumes (NO_2) when mixed with nitric oxide (§ 381).

The most striking property of nitrous oxide is its effect on the human system. If inhaled for a short time, it causes more or less nervous excitement. If breathed in large quantities, it produces temporary unconsciousness and insensi-

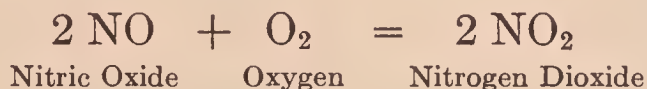
bility to pain. The gas, mixed with a small proportion of air or oxygen, is often used as an anæsthetic in dentistry.

381. Nitric oxide. — This gas is usually prepared by the interaction of copper and dilute nitric acid (sp. gr. 1.2). The equation is : —



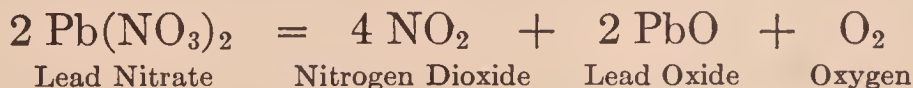
Nitric oxide is a colorless gas. It is a little heavier than air and only slightly soluble in water.

Upon exposure to air (*e.g.*, in preparing it in a test tube or flask), it combines at once with the oxygen, forming reddish brown fumes of nitrogen dioxide — a striking change. The equation is : —



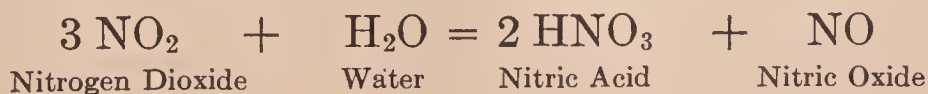
This property distinguishes nitric oxide from all other gases. It does not burn, nor support combustion, unless the burning substance (*e.g.*, phosphorus or sodium) introduced is hot enough to decompose the gas into nitrogen and oxygen, and then the liberated oxygen assists the combustion.

382. Nitrogen dioxide. — This is the reddish brown gas formed by the direct combination of nitric oxide and oxygen. It is also produced by heating certain nitrates, thus : —



The fumes of nitrogen dioxide appear when nitric acid and metals interact, but, as stated above, the nitrogen dioxide is produced by a second reaction, *viz.*, the combining of nitric oxide with the oxygen of the air.

Nitrogen dioxide has a disagreeable odor, and it is poisonous if breathed in moderate quantities. It interacts with water and yields under ordinary conditions nitric acid and nitric oxide, thus : —



It also dissolves in concentrated nitric acid, forming **fuming nitric acid**, which is a vigorous oxidizing agent.

When the reddish brown gas is cooled, it gradually loses color and at about 26°C . becomes a yellow gas. This yellow gas has the composition represented by the formula N_2O_4 and is called **nitrogen tetroxide**.

EXERCISES

1. How are (a) nitrous oxide, (b) nitric oxide, and (c) nitrogen dioxide prepared?
2. State the characteristic properties of the three nitrogen oxides.
3. What is the test for each oxide?

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

Exercise *39 — Nitric Oxide and Nitrogen Dioxide.

Exercise S36 — Nitrous Oxide — T.

TOPIC XIV: FUELS — FLAMES

383. Measurement of fuel value. — Besides the British thermal unit (B. t. u.) and the **small calorie** (cal.) (§ 235), there is another heat unit called the **large calorie** (Cal.). It is one thousand times the small calorie, and is used when the heat value is large. For example, the heat value, often called the **fuel value**, of different kinds of food is usually expressed in large calories. Thus, one gram of starch in burning gives out 4 Calories and one gram of fat 9 Calories (§ 405).

384. The calorimeter is used to find fuel value. — The fuel value of coal, charcoal, and food (dried) is measured by burning a weighed quantity of the solid in a **calorimeter**.

The essential part of the apparatus is a strong metal vessel, called a bomb, which is immersed in another vessel containing a known weight of water. The heat from the burning substance raises the temperature of the water and the rise is carefully measured by an accurate thermometer. From the weight of the substance, the weight of the water, the

rise in temperature, and certain allowances for the apparatus itself, the fuel value of the substance can be computed.

385. Producer gas. — This is made by forcing air (sometimes together with steam) through a deep coal (or coke) fire in a special kind of furnace (§ 65, Fig. 168). If steam is used, the gaseous product contains 25 to 30 per cent of carbon monoxide, 50 to 60 per cent of nitrogen, and 10 to 13 per cent of hydrogen. Its fuel value is rather low, about 145 B. t. u. per cubic foot, though it varies with the process. Producer gas is used as a fuel in many industrial and metallurgical operations. (See also § 65.)

386. Water gas. — This is made by forcing steam through a thick bed (6 or 7 feet) of hot coke or anthracite coal. It contains hydrogen and carbon monoxide — from 40 to 50 per cent of each — and is used to some extent as fuel. More often it is enriched by spraying in petroleum oil, and then used as an illuminant. If used as fuel, enriched water gas has a fuel value of 500 to 600 B. t. u. per cubic foot.

387. Manufacture of water gas. — The essential parts of the apparatus are shown diagrammatically in Fig. 169. (1) Air is forced by a blower (*A*) through the fire in the generator (*B*), the hot gases pass down the carburetor (*C*), up into the superheater (*D*), and escape through an opening (not shown) into the air. This operation is called the “blow.” It heats the fire brick inside the carburetor and superheater intensely hot; air is often forced in to raise the temperature.

(2) The air valves and the opening at the top of the superheater are now closed, and the “run” begins. Steam is forced into the generator

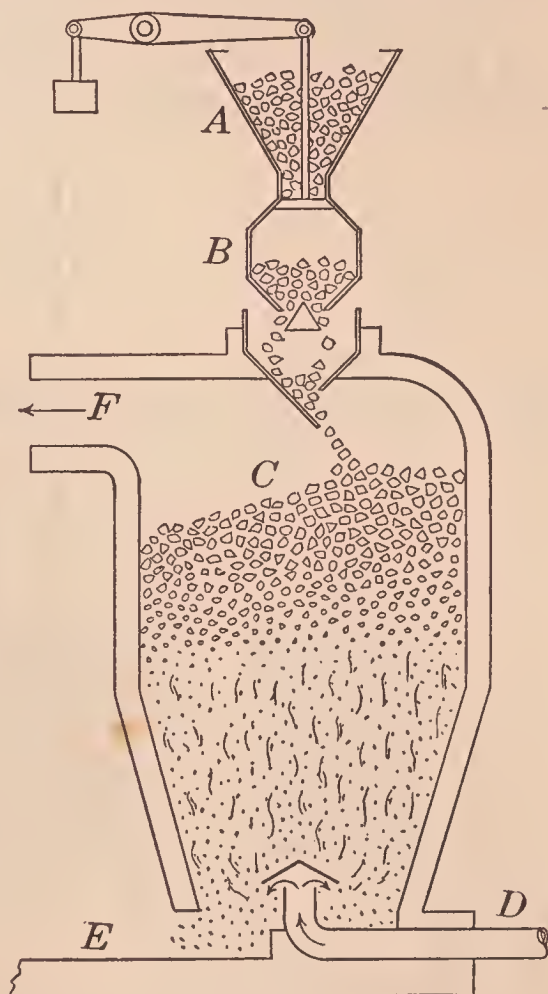
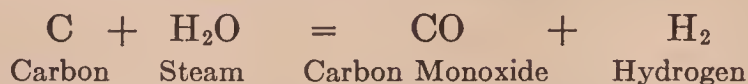


FIG. 168. — Sketch of furnace for making producer gas. Coal enters through *A*, *B*, and air through *D* into *C*. Producer gas escapes through *F* and ashes are removed at *E*.

at the bottom. In passing through the mass of incandescent carbon, the steam and carbon interact thus: —



The mixed gases rise to the top of the carburetor, where they meet a spray of oil. And as the gaseous mixture passes down the carburetor and up the superheater, the hydrocarbons (§ 246) of the oil are transformed by the intense heat into gaseous hydrocarbons which do not liquefy when the final gas is cooled.

(3) From the superheater the water gas passes through the purifying apparatus (*E*) into a holder. A ton of hard coal yields about 44,000 cubic feet of enriched water gas.

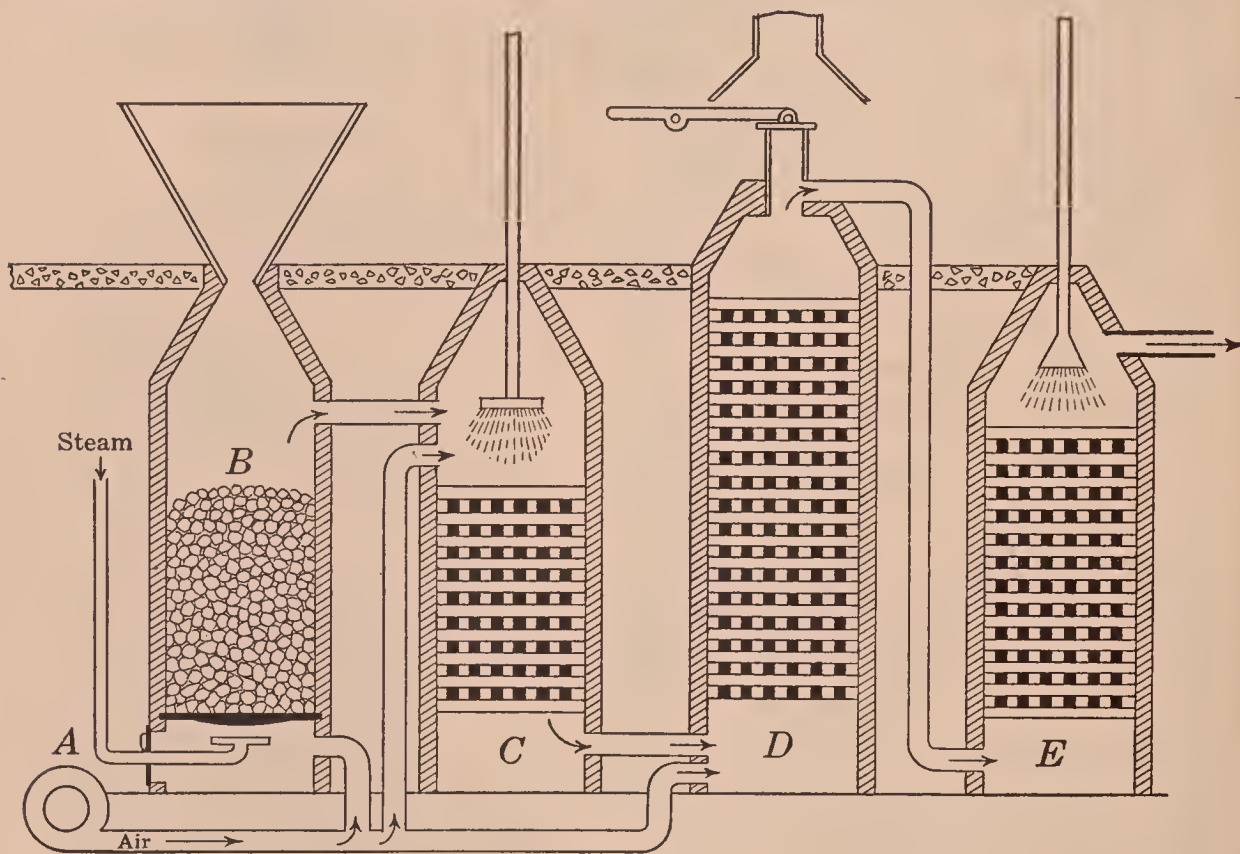


FIG. 169. — Diagram of water gas plant.

388. The illuminating gas flame. — In an ordinary illuminating gas flame (Fig. 170) the gas issues from a slit in the burner tip and spreads out in a thin layer. When the gas is ignited, the hydrocarbons decompose and the products burn; the hydrogen burns to water and part of the carbon burns to carbon dioxide. Some of the fine particles of carbon do not burn at once, but are heated hot and make the flame luminous. Eventually all the carbon burns, if sufficient oxygen is supplied and the temperature is high enough.

The flame smokes or deposits free carbon, if the air supply is cut off or diminished, or the temperature reduced. For example, if a bottle is held low down over the flame, smoke is given off; the same result is produced when the flame is cooled. The presence of unburned carbon in the flame can be shown by putting a piece of crayon or a glass rod in or just over the flame; a deposit of soot (carbon) soon gathers.

The flame is flattened to expose a large surface to the air so that all the carbon will be consumed, and thereby increase the lighting surface.

There are two distinct parts, or zones, to this flame (Fig. 170). The lower part near the tip is black and consists largely of cold, non-luminous gas, while the upper part — “the flame” — is yellow-white and contains luminous particles of carbon.

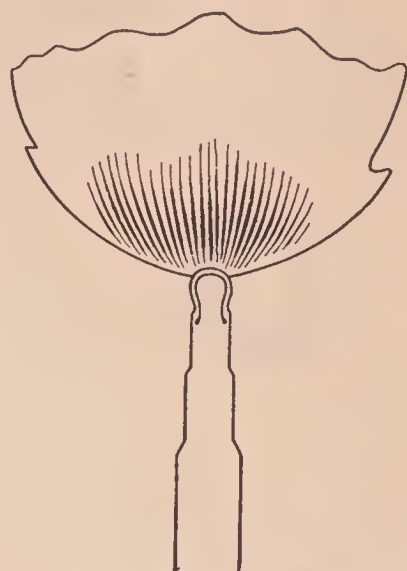


FIG. 170. — An illuminating gas flame.

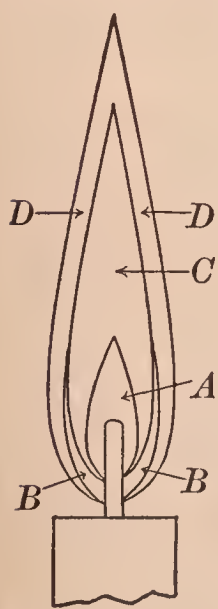


FIG. 171. — Sketch of the parts of a candle flame.

389. Other luminous flames. — In an oil lamp, *e.g.*, kerosene lamp, the oil is drawn up through the wick and volatilized by heat into a gas, which burns; the air supply is increased through small holes in the burner (below the flame) or in large lamps through a central vent also. In many lighthouses the vapor from oil is burned directly (*i.e.*, not through a wick as formerly). In a candle, the heat from the burning wick melts and volatilizes the wax, and this gas burns. The structure of luminous flames is essentially alike.

390. The candle flame. — Examination of the sketch in Fig. 171 reveals four somewhat conical portions: —

(1) Around the wick there is a dark cone (*A*), filled with combustible, but unburned, gases formed by the decomposition of the carbon compounds in the melted wax.

(2) Around the lower part of the dark cone is a faint

bluish cup-shaped part (*B, B*). It is the lower portion of the exterior cone (*D, D*).

(3) Above and surrounding the dark cone is the luminous portion (*C*). It is the largest and most important part of the flame. Combustion is incomplete here, because little oxygen can pass through the exterior cone. The hydrocarbons undergo complex changes. The most characteristic change is the liberation of small particles of carbon. This carbon, heated to incandescence by the burning gases, makes the flame luminous.



FIG. 172. — Charred paper showing the hottest part of a candle flame.

(4) The exterior cone (*D, D*) is almost invisible. Here the combustion is complete, because oxygen of the air changes all the carbon to carbon dioxide. It is the hottest region of the flame, for by pressing a piece of stiff white paper for an instant down upon the flame almost to the wick the paper will be charred by the hot outer portion of the flame (Fig. 172).

The gaseous products of the combustion of a candle are water vapor and carbon dioxide. A bottle held over a burning candle has, at first, a deposit of moisture on the inside; and if the bottle is removed and calcium hydroxide solution is added, the presence of carbon dioxide is shown by the cloudiness of the solution.

We can readily show with a candle flame how the luminosity of hydrocarbon flames is affected by temperature. Thus, if a coil of copper wire is lowered upon a candle flame, the flame smokes, loses its yellow color, and finally goes out; but if a coil of hot wire is used, the flame burns unchanged (Fig. 173).

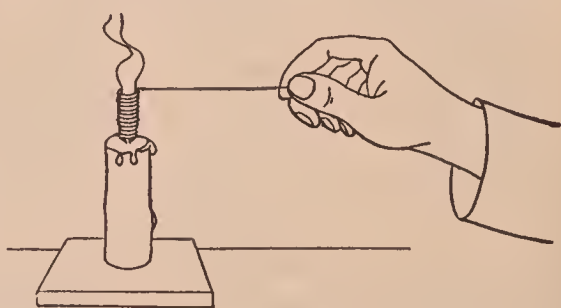
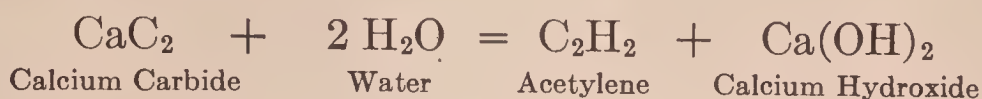


FIG. 173. — Effect of lowering the temperature of a candle flame.

It should be noted that not all luminous flames are hydrocarbon flames. Thus, magnesium burns with a brilliant flame. Its luminosity is due to the incandescence of solid particles of magnesium oxide.

Hence the use of magnesium in fireworks, *e.g.*, star shells. Similarly, the bright flame of burning phosphorus is accounted for by the incandescent particles of solid phosphorus pentoxide (Fig. 182).

391. Acetylene and its flame. — Acetylene (C_2H_2) is a gas which is prepared by the interaction of calcium carbide and water, thus : —



It can be prepared in this way for use on a small scale, as in a miner's lamp or portable lantern, or on a large scale for lighting towns, houses, caves, and mining camps.

Acetylene burns with a luminous, smoky flame. But when considerable air is mixed with the gas as the latter issues

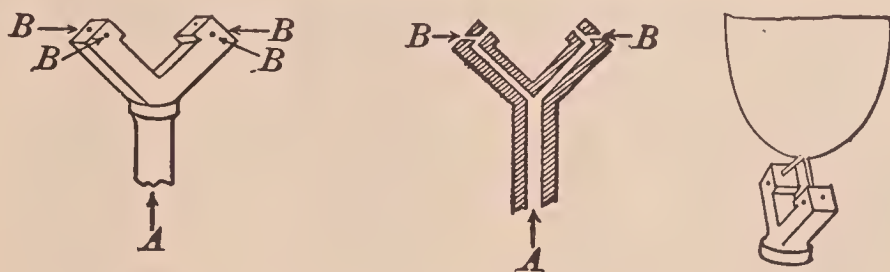


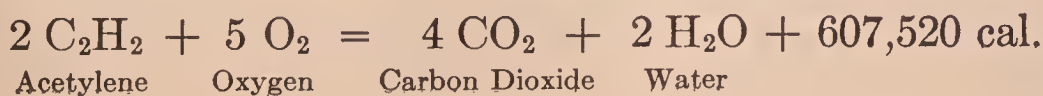
FIG. 174. — Acetylene burner and flame.

from a small opening, the mixture burns with a brilliant, white flame, which does not smoke.

A common form of acetylene burner is shown in Fig. 174. The acetylene as it escapes from the supply pipe (A) into the burner sucks in air through the small side holes (B). This mixture, upon ignition, burns as a small flat flame at right angles to the burner (Fig. 174, right).

392. The oxy-acetylene flame. — A mixture of acetylene and the proper proportion of oxygen burns with an intensely hot flame; a temperature of nearly 3500°C . can be reached if the mixture is burned by a special blowpipe called an oxy-acetylene torch (Fig. 175).

The thermochemical equation is : —



The oxy-acetylene flame is utilized in “cutting” and welding metals (Fig. 176). (See § 35.)

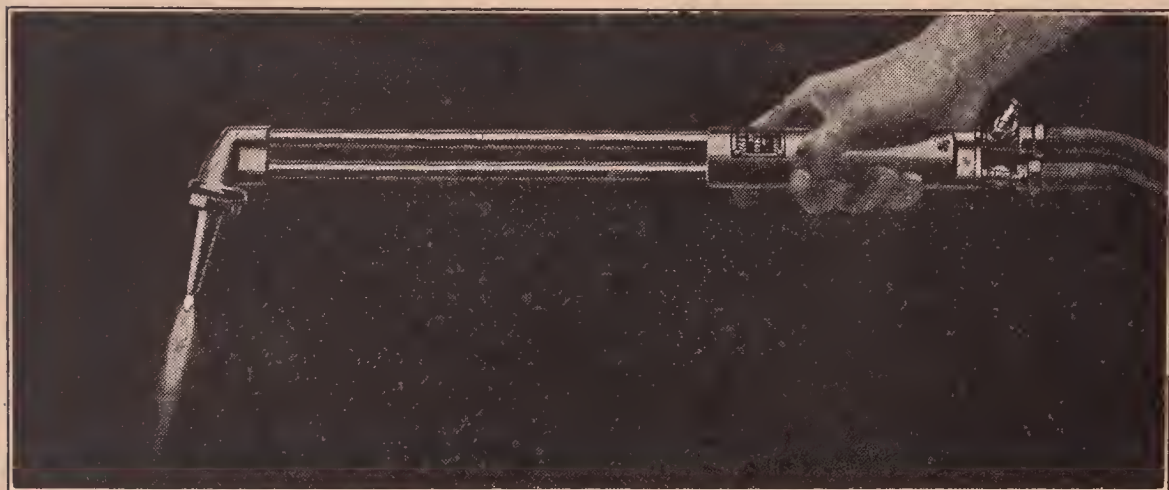


FIG. 175. — Oxy-acetylene torch and flame.

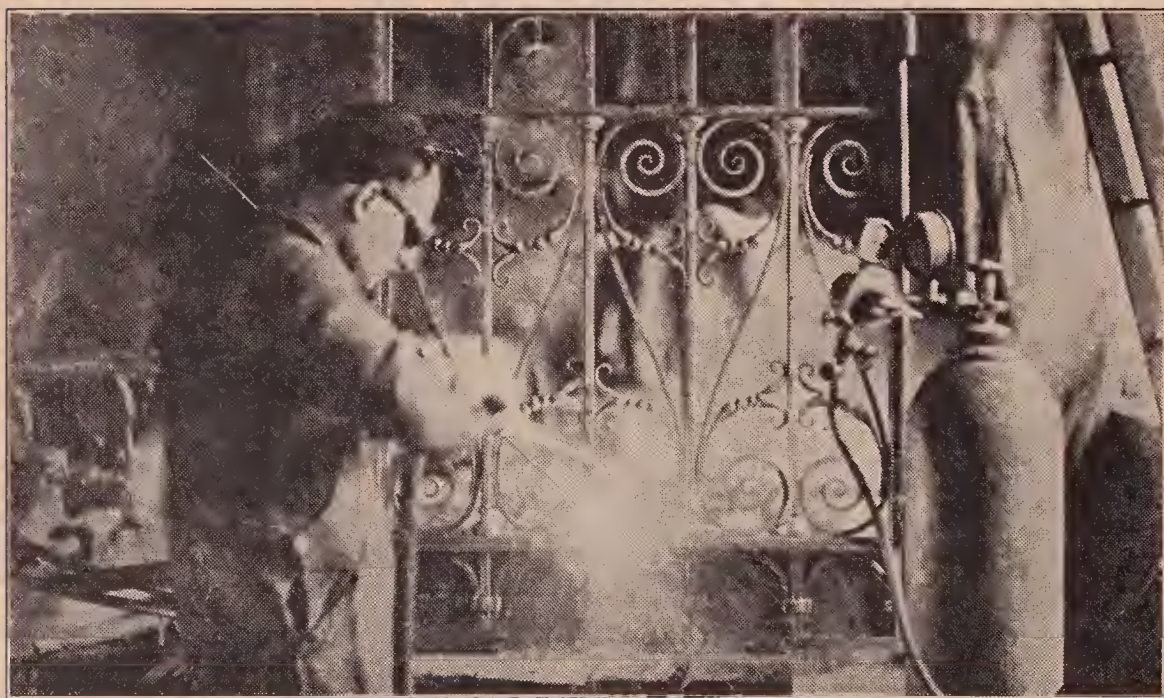


FIG. 176. — Welding an iron grill with an oxy-acetylene flame.

EXERCISES

1. What is (a) a British thermal unit, (b) a small calorie, and (c) a large calorie? What is the abbreviation of each?
2. What is producer gas? How is it made? State some of its advantages as a fuel.
3. Apply Exercise 2 to water gas.
4. Make a sketch of (a) an illuminating gas flame and (b) a candle flame.

5. Describe the two flames from the sketch made in Exercise 4.
6. What is acetylene? Write the equation for its formation.
7. Draw an acetylene burner. Describe the flame from the drawing.
8. For what is the oxy-acetylene flame used?

PROBLEMS

1. An acetylene gas plant consumes 100 cubic feet an hour. How much calcium carbide would be used in a month of 30 days if the gas is burned an average of 5 hours a day? (1 cu. ft. = 28.317 l.)
2. Calculate the B. t. u. liberated by burning 2000 cu. ft. of producer gas.
3. How many calories are liberated by burning 520 gm. of acetylene?

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

Exercise *50 — Illuminating Gas Flame — T.

Exercise *51 — Candle Flame — T.

Exercise S40 — Acetylene — T.

TOPIC XV: SOAP

393. Manufacture of soap. — Soap is made by boiling fat, or oil, with sodium hydroxide solution. This process is called **saponification**. Sodium hydroxide produces hard soap, which is a mixture chiefly of sodium palmitate, sodium stearate, and sodium oleate.

Most soaps are made by boiling the fat, or oil, and alkali in a huge kettle (Fig. 177). This operation produces a thick, frothy mixture of soap, glycerin, and alkali. At the proper time salt is added, thereby causing the soap to separate and rise to the top. The liquid beneath is drawn off, and from it glycerin is extracted.

Some soaps are boiled again, and then mixed (if desired) with perfume, coloring matter, or filling material, such as sodium silicate, sand, or borax. Floating soaps are made by forcing air into the semi-solid mass before cooling. Flake soaps are made by driving off the water from a thin layer of soap solution and scraping off the dried soap. The best soaps are prepared so that the finished product will be free from unchanged fat or "free alkali," *i.e.*, sodium hydroxide.

394. The cleansing action of soap. — This is ascribed to two causes: (1) Soap hydrolyzes, *i.e.*, interacts, with water

— especially hot water — and the liberated alkali (sodium hydroxide) acts upon the grease and oil that is usually mixed with the dirt. (2) Soap causes fat and grease to form a colloidal suspension (§§ 95, 261, 446); the minute globules remain suspended in water and adsorb the dirt, and the whole can be readily washed off. The second cause is the more efficient.

395. What is soap? — Soap is an ester, *i.e.*, a compound related to alcohols and organic acids. Thus, a simple ester

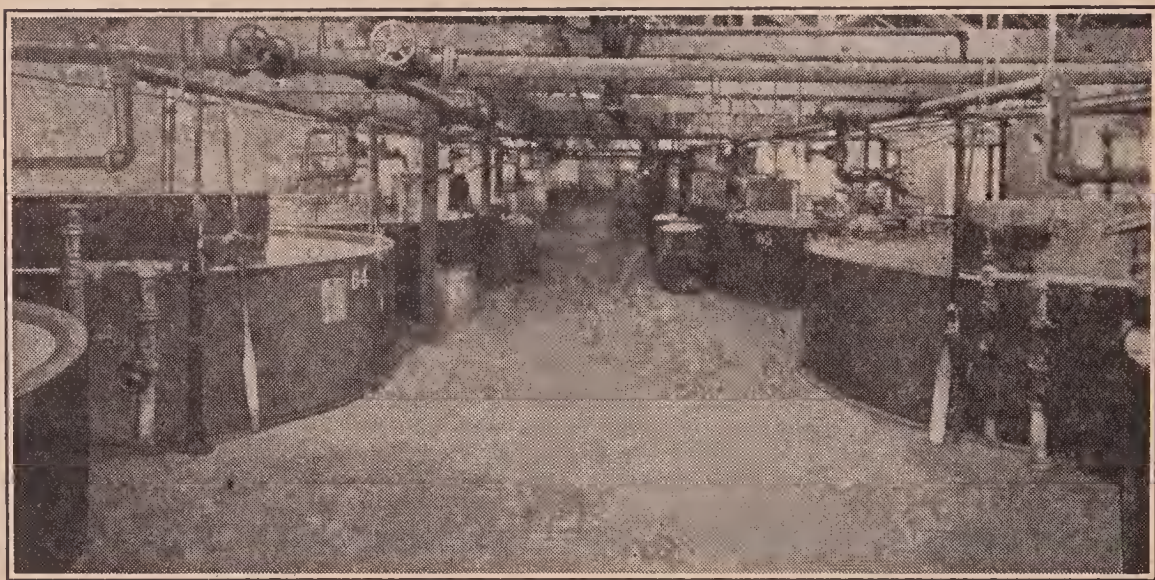


FIG. 177. — Soap kettles filled with a boiling mixture of fat and sodium hydroxide.

is ethyl acetate ($\text{CH}_3\text{COOC}_2\text{H}_5$) which is formed by heating a mixture of ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$) and acetic acid (CH_3COOH) (with a little concentrated sulfuric acid — § 264). Soap is a mixture of several esters, mainly glyceryl stearate and glyceryl palmitate.

Some **esters** occur in flowers and fruits and in many cases give the fragrance and flavor. Many are manufactured for use in perfumery, candy, beverages, and cosmetics. A common ester is methyl salicylate, which has the flavor of wintergreen.

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

Exercise S42 — Soap.

Exercise S41 — Esters.

TOPIC XVI: CELLULOSE — CELLULOSE DERIVATIVES — PAPER

396. Cellulose. — This substance forms the cell walls of plants, and is, therefore, widely distributed. Wood consists largely of cellulose. The fibers of cotton, flax, and hemp plants are nearly pure cellulose, and from them are obtained cotton, linen, and hemp. The best qualities of filter paper are nearly pure cellulose.

Cellulose is an inactive substance. It is insoluble in most liquids, and when eaten as a part of vegetables and grains,



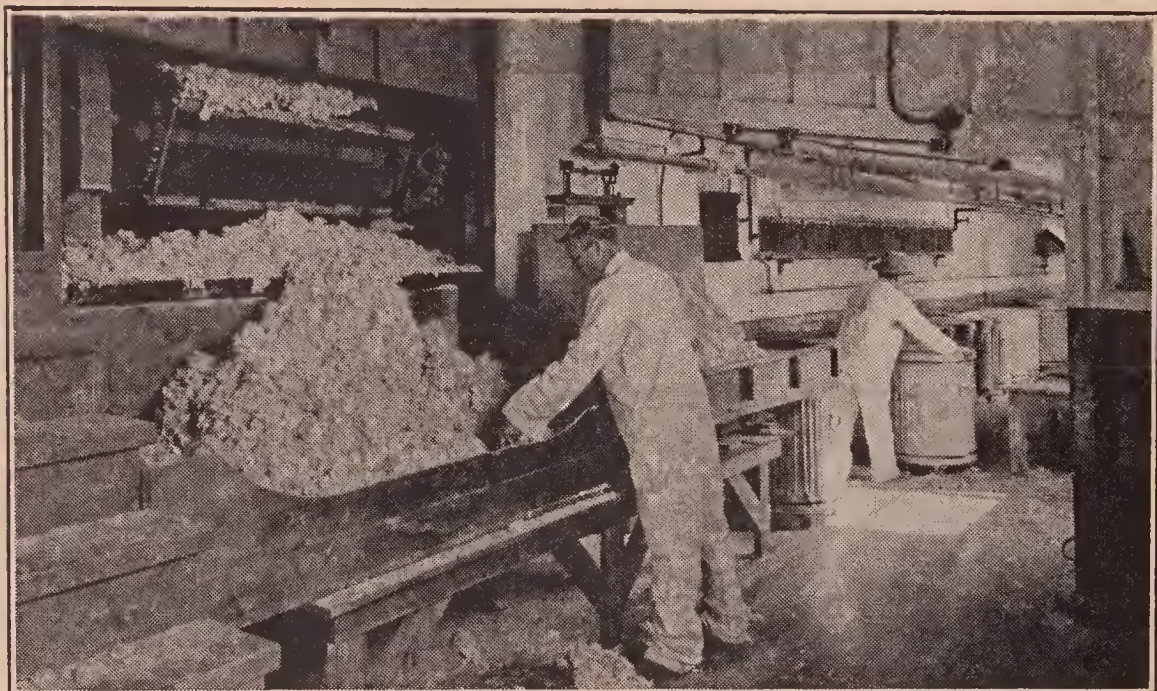
FIG. 178. — Scene in a rayon mill.

it passes through the body unchanged. It is soluble in a mixture of ammonia and copper hydroxide, and is reprecipitated by sulfuric acid of a special strength. If the solution is pressed through small holes into the acid, long shiny threads of rayon are obtained (Fig. 178). In another process, cotton or wood pulp is treated with sodium hydroxide and carbon disulfide; the product, called viscose, is dissolved and formed into threads by pressing it through dies into special solutions. If pressed through a slit, a sheet is obtained, called cellophane, which is widely used as a wrapping for fruit, candy, and food.

397. Derivatives of cellulose. — With nitric acid cellulose forms cellulose nitrates (Fig. 178a.). One is gun cotton.

It looks like ordinary cotton, and may be spun, woven, and pressed into cakes. It burns quickly, if unconfined, but when ignited by a percussion cap or when burned in a confined space, gun cotton explodes violently. It is used in blasting to some extent and especially for torpedoes and submarine mines.

A mixture of gun cotton, ether, and alcohol soon becomes a plastic mass, which upon being rolled and carefully dried forms a transparent solid called **smokeless powder**. When



Courtesy Eastman Kodak Co.

FIG. 178a. — Washing and drying cotton preparatory to changing it into cellulose nitrate.

exploded, it forms carbon dioxide and monoxide, nitrogen, hydrogen, and water vapor — all colorless gases; hence the name smokeless powder.

A solution of certain cellulose nitrates in a mixture of alcohol and ether is called **collodion**. When collodion is poured or brushed upon a glass plate or the skin, the solvent evaporates, leaving behind a thin film. It is used in preparing photographic films and as a coating for wounds.

Nitrocellulose is also an essential ingredient of special solutions called **lacquers**, which are extensively used for finishing automobiles, airplanes, furniture, and metals.

A mixture of camphor and cellulose nitrates is called **celluloid**, which is widely used in making photographic films. Colored varieties are made into ornamental objects and toilet articles. Non-breakable glass for windshields, elevator doors, etc., is made by putting sheets of celluloid between sheets of glass.

With a derivative of acetic acid, cellulose forms **cellulose acetate**, which is a transparent, tough, waterproof solid. It is non-combustible, and is made into motion picture films, coating for air-plane wings, and waterproof wrappings.

398. Paper. — This consists chiefly of cellulose fibers matted, or interlaced, together. Most paper, especially that used for newspapers, is made from wood. The best qualities of paper are made from rags.

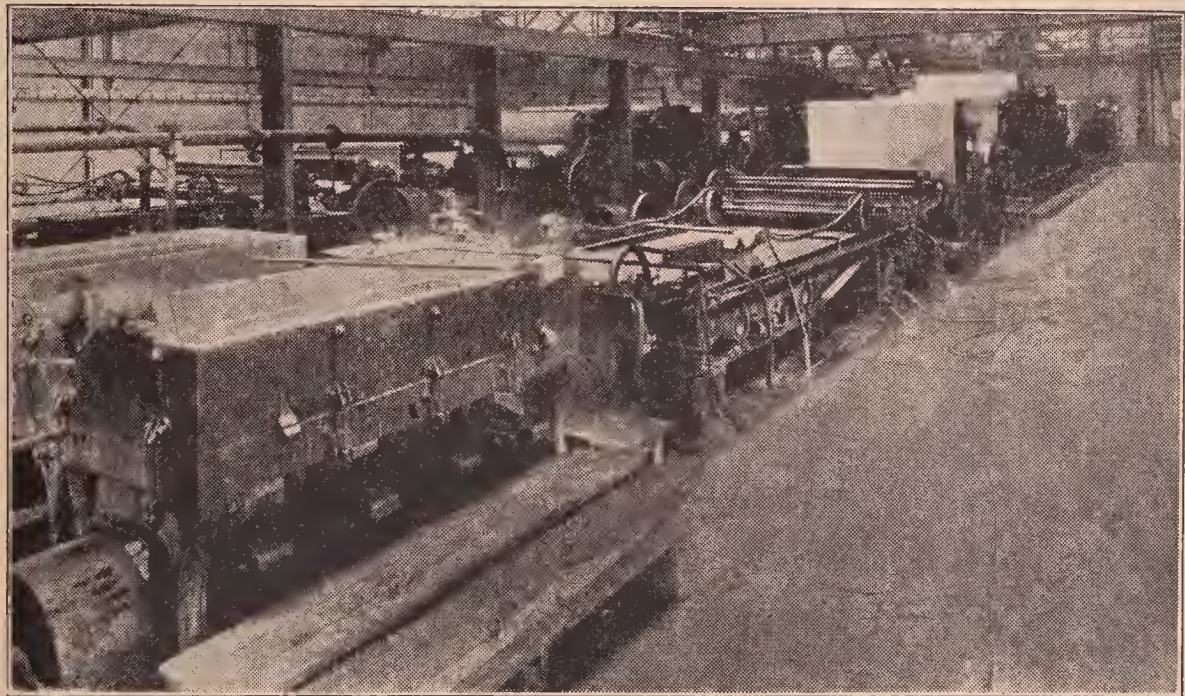


FIG. 179. — The long machine called a Fourdrinier machine for making paper.

In making paper from wood, the wood is first reduced to a pulp by grinding the wood upon a revolving stone or by heating it under pressure with sodium hydroxide or calcium bisulfite (acid calcium sulfite). The pulp is carefully washed, bleached, and washed again. It goes next to the beater in which revolving knives separate and cut the fibers of cellulose into finer particles. Here the filler (clay), sizing (rosin), and coloring matter (if desired) are added and thoroughly mixed with the pulp. Sometimes this mixture is further treated in a refiner. The pulp, thus prepared, is suspended in a large volume of water (90 to 96 per cent) and

the thin mixture is pumped to the Fourdrinier machine on which the sheet is made (Fig. 179). The pulp mixture flows on to a fine wire cloth which moves slowly along; the water drains off and leaves the fibers on the wire as a thin moist layer, which is dried and pressed by hot rollers into a compact sheet.

TOPIC XVII: FOOD AND NUTRITION

399. The functions of food. — Food has two main functions. First, it **supplies materials** needed for the growth, maintenance, and repair of the body. Second, it **provides energy** necessary to keep the body at the proper temperature, as well as to enable us to move about and perform our work.

400. Nutrients. — The parts of the food that nourish the body are called **nutrients**. And the complex process by which the nutrients become of use is called **nutrition**. Nutrients are chiefly derived from three groups of organic compounds, *viz.*, carbohydrates, fats, and proteins.

Starch and sugar are carbohydrates; nearly 70 per cent of our food is some form of carbohydrate. Butter, lard, and oils are examples of fats. Lean meat, eggs, milk, cheese, peas, beans, and grains contain protein.

Water and inorganic substances (mineral matter), though not nutrients, are vitally connected with nutrition.

401. Uses of nutrients. — Carbohydrates and fats are compounds of carbon, hydrogen, and oxygen. By digestion they are changed chemically into substances which can be oxidized readily. Thus, they provide energy, which is liberated partly as heat. They are **fuel foods**.

On the other hand proteins are **body builders**, *i.e.*, they furnish material for new tissue and ultimately replace worn-out muscle and nerve tissue. Proteins also furnish some energy, because part of their carbon and hydrogen is oxidized. They differ from carbohydrates and fats in being composed partly of nitrogen.

402. Function of water and mineral matter. — Water and mineral matter do not build tissue or furnish energy. **Water** makes up about 70 per cent of the weight of the body. It keeps the tissues soft and pliable, dissolves juices and digested

food, and assists in eliminating poisonous matter from the body.

Although **mineral matter** makes up only about 4 per cent of the weight of the body, it is indispensable for life processes. The mineral matter in the body supplies the materials for the rigid parts of the body, *e.g.*, bones and teeth, and furnishes acids, bases, salts, and organo-metallic compounds, which give many fluids and juices of the body vital properties. Hydrochloric acid of the gastric juice and the hematin of the red blood corpuscles are examples of necessary mineral matter. Mineral matter is obtained from vegetables and fruits and from seasoning added to food.

403. Composition of foods. — The average composition (in per cent) of the edible portion of some common foods is shown in Fig. 180 and also in Table XV.

TABLE XV. — COMPOSITION OF FOODS (IN PER CENT)

FOODS	WATER	CARBO- HYDRATE	FAT	PROTEIN	MINERAL MATTER
Apples	84.6	14.2	0.5	0.4	0.3
Bacon	20.2	—	64.8	9.9	5.1
Beans (dried)	12.6	59.6	1.8	22.5	3.5
Beefsteak (sirloin)	61.9	—	18.5	18.6	1.0
Butter	11.0	—	85.0	1.0	3.0
Cheese (cream)	34.2	2.4	33.7	25.9	3.8
Codfish (fresh)	82.5	—	0.3	16.3	0.9
Corn (green)	75.4	19.7	1.1	3.1	0.7
Eggs	73.7	—	10.5	14.8	1.0
Grapes	77.4	19.2	1.6	1.3	0.5
Ham (smoked)	40.3	—	38.8	16.1	4.8
Mutton (forequarter)	52.9	—	30.9	15.3	0.9
Oatmeal	7.3	67.5	7.2	16.1	1.9
Peanuts	9.2	24.4	38.6	25.8	2.0
Potatoes	78.3	18.4	0.1	2.2	1.0
Rice	12.3	79.0	0.3	8.0	0.4
Tomatoes	94.3	3.9	0.4	0.9	0.5
Walnuts (English)	2.5	16.1	63.4	16.6	1.4

404. Food as a source of energy. — The food we eat undergoes complex chemical changes in the body. These

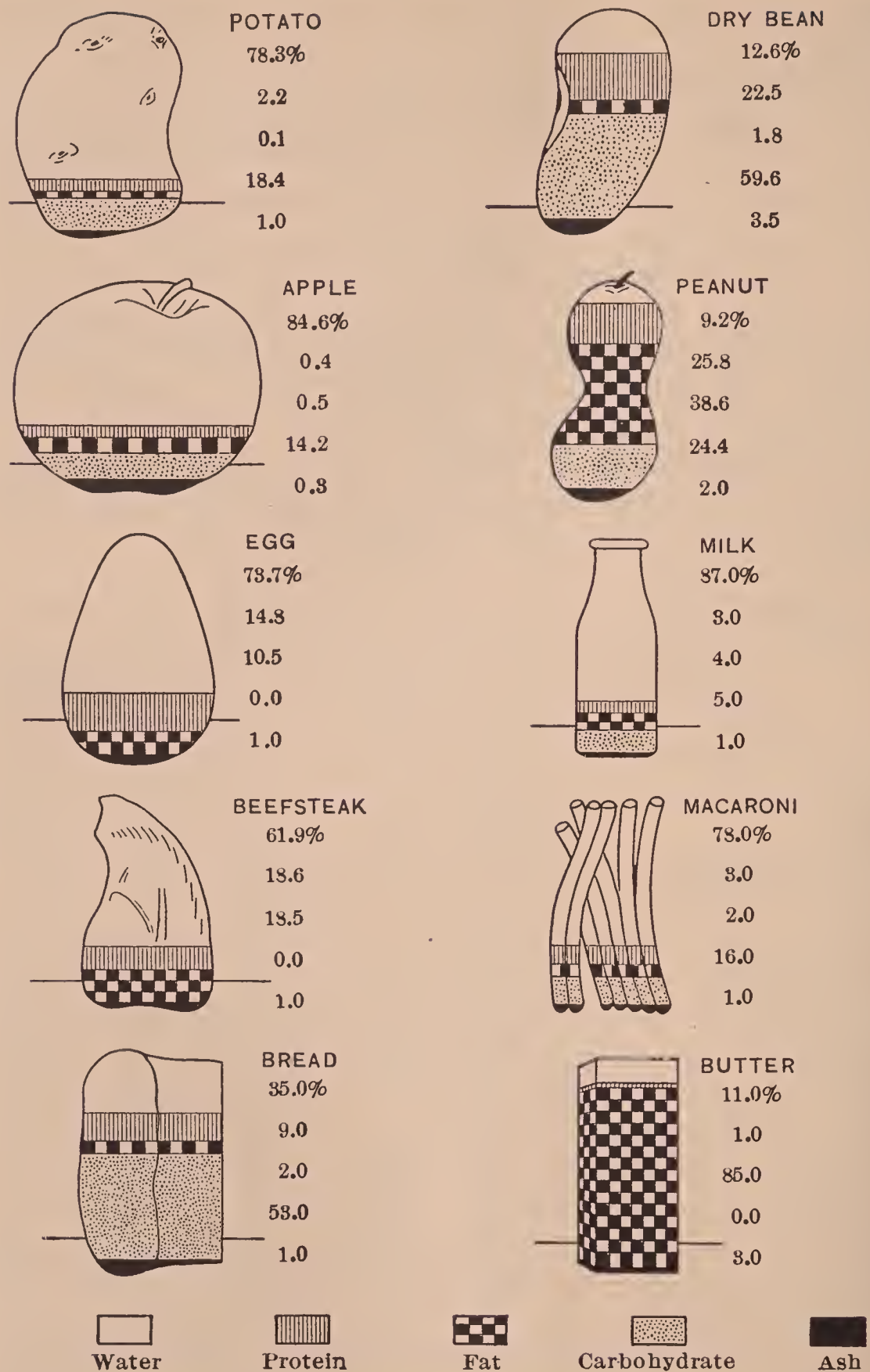


FIG. 180. — Average composition of common foods.

changes take place at first in the digestive organs and constitute the process called **digestion**. The digested food, which is in a liquid or dissolved form, is absorbed and transported to the various parts of the body, where it is built up into the tissue of which the various organs consist.

The tissues are constantly undergoing oxidation or some related process. Oxygen for this purpose comes from the air we breathe into the lungs; here the oxygen combines with the hæmoglobin of the blood and in this loosely combined form is distributed by the blood to the organs and muscles of the body. The worn-out tissue and products of digestion are slowly transformed by the oxygen into carbon dioxide and water (§ 34).

Heat is liberated by these chemical changes. We might call food a fuel, because its digested products are oxidized, just as fuels are oxidized when they burn. The heat-producing power of food is called its **fuel value**. And just as different fuels differ in the amount of heat liberated per pound, so various foods differ in their fuel value.

405. Fuel value of food. — The fuel value of food is found by burning a weighed quantity of the food in a bomb calorimeter and measuring the amount of heat liberated (§ 384). The unit used in measuring the fuel value of food is the large Calorie (Cal.). This is the amount of heat that will raise the temperature of 1 kilogram of water 1° C.

Not all the food we eat, however, is digested nor is the nutritive portion completely transformed in the body. Hence the heat values of uneaten food obtained by the bomb calorimeter must be changed a little to make up for these losses. These corrected fuel values are called **physiological fuel values**. They are the fuel values of the part of the food that is actually transformed into energy in the body — the real fuel value of the food digested and transformed. The physiological fuel values are the ones usually meant when the term fuel value is used.

The fuel value of food is often stated in Calories per pound, *i.e.*, the number of Calories furnished by one pound of food. The fuel values of the foods tabulated in § 403 are shown in Table XVI.

TABLE XVI. — FUEL VALUE OF FOODS
(CALORIES PER POUND)

Apples	290	Codfish	325	Oatmeal	1860
Bacon	2840	Corn	470	Peanuts	2560
Beans	1605	Eggs	720	Potatoes	385
Beefsteak	1130	Grapes	450	Rice	1630
Butter	3491	Ham	1940	Tomatoes	105
Cheese	1950	Mutton	1595	Walnuts	3285

406. How much food do we need? — The amount of food needed varies with many factors, *e.g.*, weight, work, age, and sex. A growing boy needs more than his father, a football player more than one who watches the game, and a hard laborer more than one who has a sedentary occupation. An average adult man who does moderate muscular work needs enough food to yield from 2500 to 3000 Calories a day. A satisfactory division among the nutrients would be:—

Carbohydrate	400–500 gm., or	1600–2000 Cal.
Fat	70–85 gm., or	630–765 Cal.
Protein	75–80 gm., or	300–320 Cal.

An average adult woman needs from 2000 to 2500 Calories a day.

The fuel value of food is only part of the story. Sugar or butter would furnish enough heat, but a diet consisting largely of carbohydrates or fats would not repair worn-out tissue. We must eat food containing protein, as well as carbohydrates and fat. Authorities agree that an adult who does moderate muscular work needs 75–80 grams (3 ounces) of protein per day. If more is eaten, it is partly consumed as fuel and partly rejected by the body.

The amount of food we need, stated in Calories, can be estimated from Table XVII, which shows the approximate expenditure of energy (in Calories) per hour. This table itemizes the energy (in Calories) given out, so to speak, by a healthy man or woman weighing 154 lb. and 123 lb. respectively. By adding the Calories for the different items we

can get the approximate value of the food we must eat per day to give this energy.

TABLE XVII. — APPROXIMATE EXPENDITURE OF ENERGY
IN CALORIES PER HOUR

Sleeping	60-70	Walking, slowly	200
Awake, lying still	70-85	Moderate exercise	240
Sitting, at rest	100	Walking, actively	300
Standing, at rest	115	Hard exercise	480
Typing, rapidly	140	Running	500

407. Vitamins. — Vitamins are present in food in minute amounts yet they are essential to growth and good health. Our diet should always include certain foods which furnish vitamins, especially milk, leaf vegetables, unpolished cereals, and fruit juices. There are several types of vitamins, but we can consider only the following: —

(1) Vitamin A, or fat-soluble A, occurs in butter, milk, egg yolk, cod liver oil, and spinach. It is not found in meats (to any extent), nuts, sugars, or oils from plants. Vitamin A contributes to general vigor and health. It is especially needed to promote the growth of children.

(2) Vitamin B, or water-soluble B, occurs in yeast, nuts, fruits, spinach, tomatoes, and the outer coating of rice and other grains. It is not found in refined flour. Vitamin B is essential to normal nutrition. Its lack leads to stunted growth.

(3) Vitamin C, or water-soluble C, occurs in lemons, oranges, tomatoes, cabbage, lettuce. Nuts, meats, and grains (especially refined ones) contain little or none. Vitamin C prevents and cures scurvy.

408. How to select an adequate diet. — By means of Table XVIII it is easy to arrange several sets of daily menus which will furnish sufficient fuel value and include the approximate amount of protein. By learning the fuel value and protein content of the important items, or those used frequently, we can readily tell if the diet is adequate.

TABLE XVIII. — SERVINGS OF FOOD

FOOD	WEIGHT IN GRAMS				TOTAL CALO- RIES
	Average Serving	Protein	Fat	Carbo- hydrate	
Apple, baked	135	1	1	26	117
Apple, raw	150	0.5	0.5	16	70
Banana, raw	194	1.5	0.8	28	125
Beans, baked	185	19	9	47	345
Beets (4 heaping Tbs.) . .	200	5	—	15	80
Biscuit (3 baking powder) .	90	8	11	45	311
Bread, white (2 slices) . .	76	6.5	1.5	40	200
Butter	15	0.2	13	—	118
Cheese (1 cu. in.)	20	6	7	—	87
Chicken, creamed (on toast)	125	17	13	22	273
Cocoa, 1 cup	230	5	6	12	122
Codfish cakes (2)	132	19	3	17	171
Corn chowder (1.5 cups) . .	333	10	10	39	286
Cream of wheat	250	5	1	33	161
Cream toast (1 slice) . . .	148	11	11	49	339
Custard (2 heaping Tbs.) .	134	7	8	19	176
Doughnut (1)	37	2.5	8	20	162
Dressing, French (2 ts.) . .	9	—	7	—	63
Egg (1)	50	6.5	6	—	80
Figs (5)	100	4	0.3	73	309
Fish chowder (1 cup) . . .	284	38	10	30	362
Fish, stuffed and baked . .	152	33	4	7	196
Hominy (1 cup)	245	3	—	32	140
Ice cream (2 heaping Tbs.) .	100	5	10	18	182
Lamb, roast (1 slice) . . .	90	20	27	—	323
Lettuce, 4 leaves	50	1	—	1	8
Macaroni and cheese (1 cup)	200	10	14	32	294
Milk and sugar for cereal . .	73	2	2	15	86
Milk, glass	220	7	9	11	153
Onions, boiled	85	2	—	10	48
Orange	250	1.5	0.3	21	93
Pie, apple ($\frac{1}{6}$)	126	4	12	54	340
Potato, baked	130	4	—	32	144
Potato, boiled	150	4	—	31	140
Potato, sweet	100	3	2	42	200
Prunes (5)	50	1	—	63	256
Pudding, chocolate farina .	141	7	7	33	223
Pudding, cottage	144	6	10	77	422

TABLE XVIII. — *Continued*

FOOD	WEIGHT IN GRAMS				TOTAL CALO- RIES
	Average Serving	Protein	Fat	Carbo- hydrate	
Pudding, rice	133	6	7	34	223
Rice, steamed (1 cup) . . .	200	4	—	40	176
Salad, fruit	262	2	1	46	201
Salad, potato	150	4	—	31	140
Salad, vegetable	157	3	1	16	85
Sandwich, chicken	70	9	4	22	160
Sandwich, ham	70	7	10	27	226
Shredded wheat (1)	29	3	0.5	23	108
Snow pudding (2 heaping Tbs.)	80	4.5	—	12	66
Soup, cream of celery (1 cup)	125	3	9	5	113
Soup, cream of tomato (1 cup)	125	3	9.5	6.5	123
Spinach (1 heaping Tbs.) . .	100	2	4	3	56
Steak, Hamburg (1 cake) . .	50	16	8	—	136

409. How to select a proper diet. — The carbohydrates and fats must be in the right quantity for fuel value and the protein in the proper proportion for tissue building (§ 406). Moreover, we ought to select the three classes of nutrients from a wide variety of foods in order to provide a mixed diet, obtain the right kind of protein, and secure indispensable vitamins and mineral matter. We should drink water freely — at least six glasses a day. We should eat regularly an abundance of vegetables and cereals, which yield mineral matter and furnish bulky ingredients, *e.g.*, cellulose, needed to assist the elimination of solid waste matter. Certain foods should always form a part of our diet, *e.g.*, leaf vegetables (especially spinach), milk, whole wheat, unpolished rice, and fruit because they provide vitamins.

EXERCISES

1. Define the terms *food*, *nutrition*, and *nutrients*.
2. State the composition and fuel value of (a) bread, (b) butter, (c) potatoes, (d) eggs, (e) milk.

3. Select from the table in § 403 foods rich in (a) protein, (b) carbohydrate, and (c) fat.

4. Assuming that one square inch represents 1000 Calories, draw diagrams of the fuel value of five foods from the table in § 405.

5. Use the table in § 408 for the following: (a) Make out a menu for breakfast, dinner, and supper which contains 75–80 gm. of protein and furnishes 2500–3000 cal. (b) As in (a) for 100 gm. of protein and about 3500 Cal. (c) As in (a) for 100 gm. of fat, 85 of protein, and about 4000 Cal.

6. Use the table in § 408 to keep a record (or make an estimate) of the approximate amount of carbohydrate, fat, and protein you eat in (a) one day, (b) three days, (c) one week, (d) one lunch.

7. Calculate the weight of (a) mineral matter in 1 lb. of cheese, (b) water in 1 lb. of potatoes, (c) fat in 1 lb. of beefsteak, (d) protein in 1 lb. of beans, (e) water in 1 lb. of butter, (f) carbohydrate in 1 lb. of oatmeal.

8. (a) What weight of bacon is needed to furnish as much fat as 1 lb. of butter? (b) Of tomatoes to provide the carbohydrate in 1 lb. of potatoes? (c) Of oatmeal to equal the protein in 1 lb. of beans?

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

Exercise S43 — Nutrients in Food — T.

Exercise 56 — Testing Baking Powders.

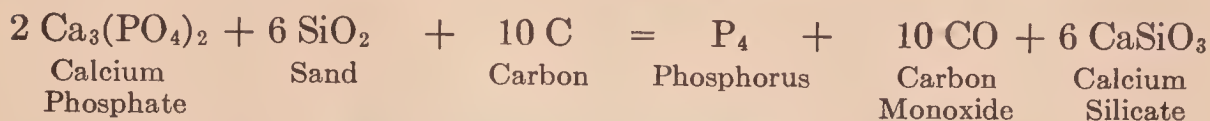
TOPIC XVIII: PHOSPHORUS — ARSENIC INSECTICIDES — ALLOYS OF ANTIMONY AND BISMUTH

410. Occurrence of phosphorus. — Free phosphorus is not found in nature, but phosphates are numerous and abundant. The most common phosphate is calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$), which is the chief ingredient of "phosphate rock" and bones (80 per cent). Small amounts of phosphates occur in fertile soils and some iron ores. Complex organic phosphorus compounds are found in the germs of seeds and the nerves, brains, and muscles of animals.

411. Manufacture of phosphorus. — Phosphorus is manufactured in an electric furnace (Fig. 181).

The mixture of calcium phosphate, carbon, and sand is introduced at *A* and fed continuously into the furnace by the screw *B*. An electric current passed between the electrodes *EE* produces the intense heat

needed for the chemical change. The phosphorus vapor escapes through *C* into a condenser; the liquid residue, which is essentially calcium silicate, is drawn off as slag at *D*. The equation is: —



The phosphorus is purified, melted, and cast into small sticks.

412. Properties of white phosphorus. — There are two kinds of phosphorus — commonly called white and red. The phosphorus prepared by the method just described is the white or ordinary form. It is a slightly yellow, translucent solid.

The color deepens by exposure to light. At ordinary temperatures it is soft like wax, and can be cut with a knife. At low temperatures it is brittle. It dissolves in carbon disulfide.

White phosphorus is a dangerous substance. When exposed to air it oxidizes quickly and gives off white fumes. At about 35° C. it takes fire, often suddenly, and burns with a brilliant flame. It must be kept beneath water and should not be touched with the hands unless it is wet. The safest way is not to touch it at all, but to use wet forceps in holding or transferring it. Unusual care should be taken not to leave bits of phosphorus in deflagrating spoons or dishes.

In moist air white phosphorus is slightly luminous. This property gave the element its name (from a Greek word meaning “light bringer”).

White phosphorus has a faint odor. The fumes are very poisonous, and cause a dreadful disease, which rots the bones, especially the jaw bones (§ 414).

White phosphorus in burning forms a cloud of white particles of phosphorus pentoxide (P_2O_5), which soon settles. In rather moist air, however, the pentoxide unites with

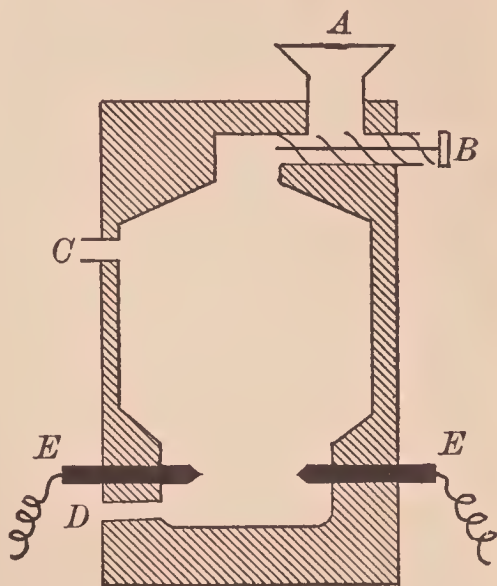


FIG. 181. — Sketch of electric furnace for the manufacture of phosphorus from calcium phosphate.

water to form phosphoric acid, which remains suspended as a fog. In the World War phosphorus was used to make a smoke screen and as an ingredient of incendiary bombs (Fig. 182).

413. Red phosphorus. — This is a red solid. - It is made by heating white phosphorus to 250° – 300° C. in a closed vessel freed from air. Red phosphorus is quite different from white phosphorus. It does not glow in the air, nor

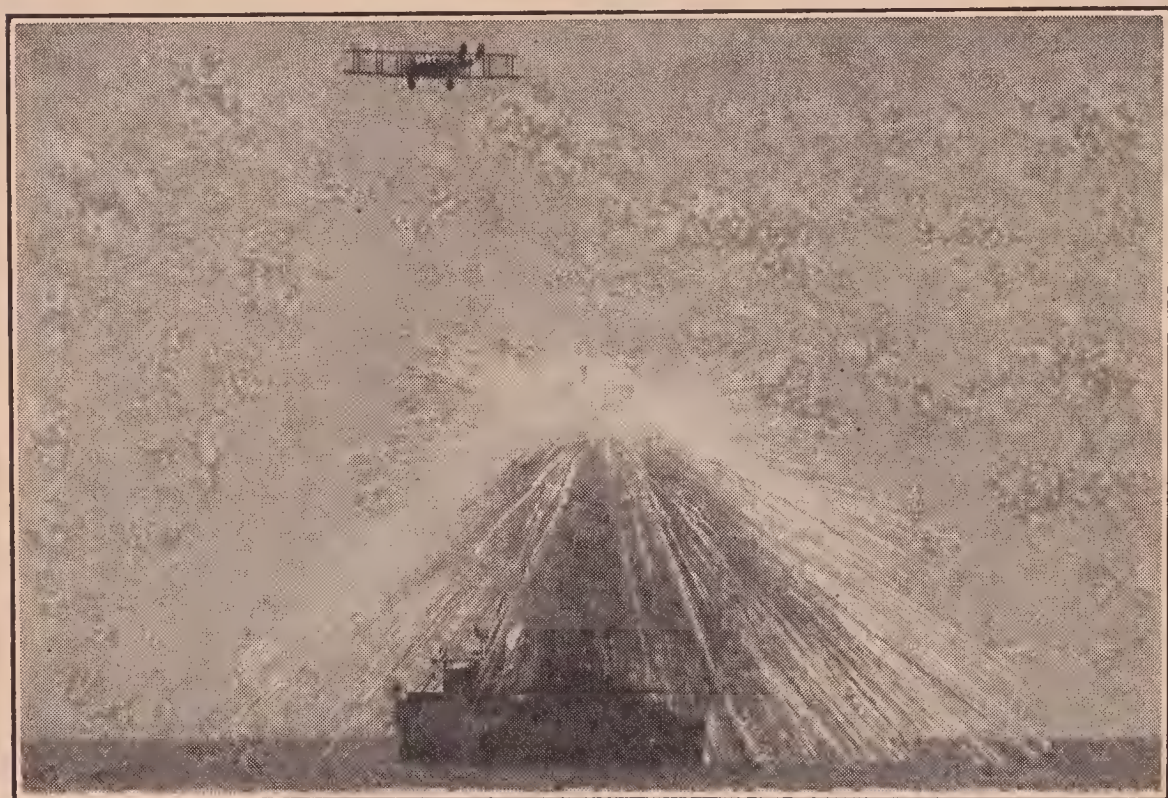


FIG. 182. — A phosphorus bomb dropped from an airplane and exploding on a warship.

does it ignite until heated to about 240° C. It is not poisonous, and does not dissolve in carbon disulfide. It does not combine with oxygen at ordinary temperatures and can be handled safely.

414. Matches. — Phosphorus was formerly used extensively in the manufacture of matches. Phosphorus sulfide (P_4S_3) is now used in the United States as a substitute for the element. This change was made on account of a prohibitive tax upon phosphorus matches (two cents per hundred matches); the tax was levied mainly to protect the workmen from the disease caused by breathing phos-

phorus fumes. The sulfide is not poisonous and is as suitable for match heads as phosphorus itself.

Ordinary matches are made by dipping one end of the match sticks first into melted paraffin and then into the "phosphorus mixture." The latter consists usually of different proportions of phosphorus sulfide, manganese dioxide or another oxidizing substance, and glue or some other binding material mixed with a little coloring matter. These matches are the **ordinary friction kind**. By rubbing them on a rough surface the friction generates enough heat to ignite the phosphorus compound, which continues to burn owing to the oxygen supplied (mainly) by the oxidizing agent. The heat thereby produced sets fire to the paraffin, and this in turn kindles the wood.

In **safety matches** the head is usually a colored mixture of antimony sulfide, potassium chlorate, and glue, while the surface on the box upon which the match must be rubbed to ignite is a mixture of red phosphorus, glue, and powdered glass.

415. Uses of arsenic compounds. — Arsenic trioxide (As_2O_3) is used to a limited extent in making fly and rat poison, glass (especially plate glass), and arsenic compounds (*e.g.*, insecticides), and for destroying weeds and preserving skins in museums.

Arsenic trioxide is a **poison**. The antidote for arsenic poisoning is fresh ferric hydroxide, which is made by adding ammonium hydroxide to a ferric salt, *e.g.*, ferric chloride. The ferric hydroxide forms an insoluble substance with the arsenic compound.

The chief use of other arsenic compounds is for destroying insects. The **insecticides**, as they are often called, are used in the form of dust or sprays. Paris green ($\text{Cu}_3(\text{AsO}_3)_2 \cdot \text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$) and lead arsenate ($\text{Pb}_3(\text{AsO}_4)_2$) are used extensively to exterminate potato bugs and other insect pests. Calcium arsenate ($\text{Ca}_3(\text{AsO}_4)_2$) is used to exterminate the boll weevil, an insect which destroys the cotton plant. It is dusted on from an airplane (Fig. 183).

416. Alloys of antimony. — Antimony and bismuth are used to make alloys. When antimony is melted with some metals, especially lead and tin, the metals dissolve one another. Such a metallic solution upon solidifying forms an **alloy**. Alloys have different, often very different, properties from the original metals. Thus, an alloy of 10 per cent



FIG. 183. — Airplane dusting a cotton field with calcium arsenate.

antimony, 70 per cent lead, and 20 per cent tin expands on cooling, and is harder than lead.

This alloy is used as **type metal**, because it makes the face of the type hard and reproduces sharply the dots and fine lines (of the mold). **Babbitt metal** contains antimony, tin, and copper. It is used for the bearings of machines to reduce friction. Other **anti-friction alloys** contain antimony, lead, tin, and a little copper. Another alloy containing an appreciable proportion of antimony is **Britannia metal**, which is used in making ornaments and table ware.

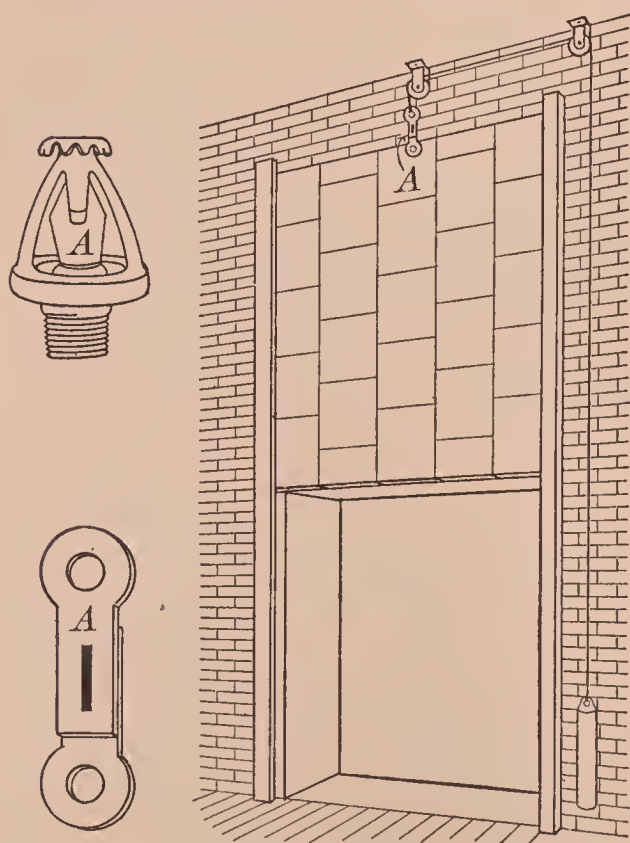


FIG. 184. — Sprinkler head, fusible link, and fireproof door (held in place by a link of fusible metal). Fusible metal is at A,

417. Alloys of bismuth. — Bismuth is used in making alloys which have

low melting points. The metal itself melts at 270°C . But alloys of bismuth, lead, and tin melt at a much lower temperature. For example, Newton's metal melts at 94.5°C . and Rose's metal at 98.3°C .; while Wood's metal, which contains the metal cadmium also, melts at only 60.5°C .

These alloys of bismuth are called **fusible metals**. They are used in making safety plugs for steam boilers, fuses for electrical appa-

ratus, and as connecting links to hold in place automatic fireproof doors and to close the heads in the automatic sprinkling apparatus frequently installed in large buildings (Figs.

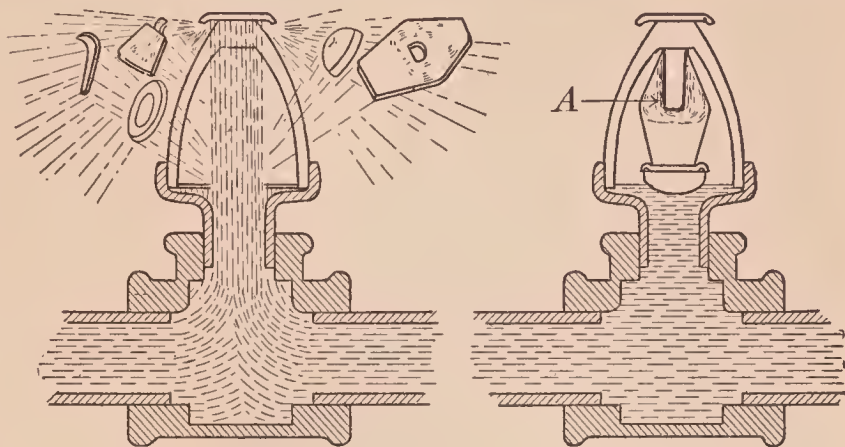


FIG. 185. — Sprinkler head — closed (right) and open (left). The parts of the dismantled head are shown (left). Fusible metal in place at A (right).

184, 185 — fusible metal at A). In case of fire, the heat soon melts the fusible metal in the sprinkler heads, thereby providing openings in the pipes from which the water flows. The fireproof door is kept open by a weight until the heat melts the fusible metal and lets the door close automatically. (Study Fig. 184.)

EXERCISES

1. Describe the manufacture of phosphorus.
2. State the properties of (a) white and (b) red phosphorus.
3. State the uses of alloys of (a) antimony and (b) bismuth.

PROBLEMS

1. Calculate the weight of phosphorus in 40 tons of calcium phosphate.
2. Calculate the percentage composition of (a) arsenic trioxide and arsenic pentoxide, and (b) antimony trichloride and antimony pentachloride.
3. How many gm. of phosphorus can be made by the electrothermal process from a ton of calcium phosphate (70 per cent pure)?

TOPIC XIX: ARRANGEMENT OF THE ELEMENTS BY
ATOMIC WEIGHTS AND BY ATOMIC NUMBERS

418. Arrangement of the elements. — Elements differ from one another in many ways. Some of them, however,

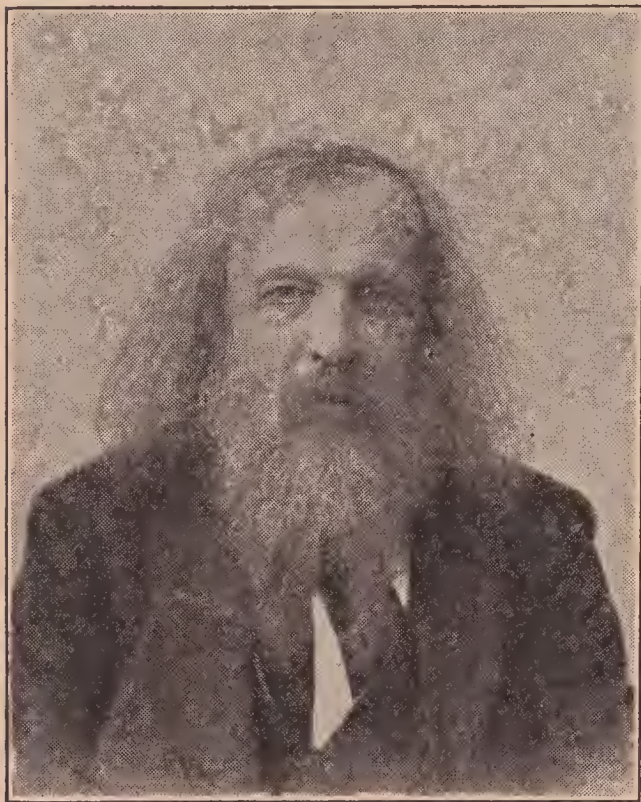


FIG. 186. — The Russian chemist Mendelejeff, who made the first systematic arrangement of the elements.

are similar in their properties and can be put into the same class. Thus, there are the large classes of metals and non-metals. Certain elements are so closely related they can be put into small groups, *e.g.*, fluorine, chlorine, bromine, and iodine (§ 440). Other elements can be similarly grouped according to their properties, *e.g.*, calcium, strontium, and barium.

419. Arrangement of the elements according to their atomic weights.

— The Russian chemist Mendelejeff (Fig. 186) was the first to show how

to arrange the elements according to a definite plan. His arrangement, which appeared in 1869, is based on the relation between the properties of the elements and their atomic weights. This arrangement was made into a table known as the periodic table of the elements. It guided chemists in their work for over half a century.

Mendelejeff's scheme of arrangement is substantially as follows: If the elements — omitting hydrogen and beginning with helium — are arranged in the order of their increasing atomic weights, a series results in which similar or closely related elements occur at definite intervals. Thus, we would have the accompanying arrangement of pairs for the first sixteen elements:

Helium 4	Lithium 7	Beryllium 9	Boron 11
Neon 20	Sodium 23	Magnesium 24	Aluminum 27
Carbon 12	Nitrogen 14	Oxygen 16	Fluorine 19
Silicon 28	Phosphorus 31	Sulfur 32	Chlorine 35.5

Examination shows, for example, that the two similar elements fluorine and chlorine occur as a vertical group, fluorine being the eighth and chlorine the sixteenth. The elements in the other groups, especially lithium and sodium, nitrogen and phosphorus, are similarly related.

An analogous relation exists among the 80 or more elements (with three exceptions), though not so typically as among the first twenty elements. The recurrence of similar elements at definite intervals means that the long series made up of all the elements breaks up into shorter series of eight, or some number near eight. These shorter series are called **periods**, and the arrangement of the elements in this way is called the **periodic arrangement**.

The fundamental relation of this arrangement, *viz.*, recurrence of elements at definite intervals, is sometimes stated thus : —

The properties of the elements vary periodically with their atomic weights.

If the long series is divided into periods and the periods are placed below each other, a table called the periodic table is obtained which is substantially like Table XIX. The horizontal rows numbered 1 to 6 are the **periods**. The vertical columns numbered 0 to VIII are the **groups**.

420. Groups and families. — Elements which resemble one another are found in the same group. In some groups certain elements are more closely related than others, giving rise to sub-groups or families. Groups and families are found in Table XIX, and the important ones should be learned.

421. The old periodic law. — Not all the periods are so typical as 1 and 2, nor are the elements in some groups so closely related as in group I. Nevertheless a careful and comprehensive study of all the elements shows that in many

TABLE XIX. — ARRANGEMENT OF THE ELEMENTS BY ATOMIC WEIGHTS

GROUP	0	I		II		III		IV		V		VI		VII		VIII
Family		A	B	A	B	A	B	A	B	A	B	A	B	A	B	
Period 1	Helium He, 4.0	Lithium Li, 6.94		Beryllium Be, 9.02		Boron B, 10.82		Carbon C, 12.0		Nitrogen N, 14.0		Oxygen O, 16.0		Fluorine F, 19.0		
Period 2	Neon Ne, 20.183	Sodium Na, 22.997		Magnesium Mg, 24.32		Aluminum Al, 26.97		Silicon Si, 28.06		Phosphorus P, 31.027		Sulphur S, 32.06		Chlorine Cl, 35.457		
Period 3	Argon A, 39.94	Potassium K, 39.10		Calcium Ca, 40.07		Scandium Sc, 45.1		Titanium Ti, 47.90		Vanadium V, 50.96		Chromium Cr, 52.01		Manganese Mn, 54.93		Iron Fe, 55.84 Cobalt Co, 58.94 Nickel Ni, 58.69
		Copper Cu, 63.57		Zinc Zn, 65.38		Gallium Ga, 69.72		Germanium Ge, 72.60		Arsenic As, 74.96		Selenium Se, 79.2		Bromine Br, 79.92		
Period 4	Krypton Kr, 82.9	Rubidium Rb, 85.44		Strontium Sr, 87.63		Yttrium Yt, 88.93		Zirconium Zr, 91.22		Columbium Cb, 93.1		Molybdenum Mo, 96.0				Ruthenium Ru, 101.7 Rhodium Rh, 102.9 Palladium Pd, 106.7
		Silver Ag, 107.88		Cadmium Cd, 112.4		Indium In, 114.8		Tin Sn, 118.7		Antimony Sb, 121.76		Tellurium Te, 127.5		Iodine I, 126.93		
Period 5	Xenon Xe, 130.2	Cæsium Cs, 132.81		Barium Ba, 137.36		Lanthanum La, 138.9		Cerium* Ce, 140.13		Tantalum Ta, 181.5		Tungsten W, 184.0				Osmium Os, 190.8 Iridium Ir, 193.1 Platinum Pt, 195.2
		Gold Au, 197.2		Mercury Hg, 200.6		Thallium Tl, 204.0		Lead Pb, 207.2		Bismuth Bi, 208.0						
Period 6	Radon Rn, 222	—		Radium Ra, 225.97		—		Thorium Th, 232.12		—		Uranium U, 238.14				

* Between Cerium and Tantalum a number of elements are omitted

cases their properties vary periodically with the atomic weight. Mendelejeff summarized these facts in a form sometimes called the **old periodic law**, thus : —

The properties of the elements are periodic functions of their atomic weights.

The term *function* as used here means the exhibition of a special relation, *viz.*, that of properties to atomic weight. Strictly speaking, the relation summarized by Mendelejeff is not sufficiently accurate to be called a law. Interpreted freely, the facts at the basis of Mendelejeff's periodic arrangement mean : (1) properties and atomic weights are related ; and (2) this relation is exhibited in many instances at regular intervals.

422. Imperfections in the old periodic arrangement. —

(1) There are vacant places (indicated by dashes). These probably correspond to elements not yet discovered. Three vacant places in the original table were filled many years ago, and recently other places were filled. (2) Three elements are out of place, *e.g.*, argon undoubtedly belongs under neon, yet its atomic weight (39.94) would necessitate its exchange with potassium (39.10) — an absurdity ! There are two other pairs of elements not located where their atomic weights demand. (3) Hydrogen lacks an acceptable place ; it really has no place ! (4) The table lays too much stress on a single valence which is not always the common valence.

There is undoubtedly a more fundamental basis for arranging the elements, *viz.*, their atomic numbers.

423. Arrangement of the elements according to their atomic numbers. — The present basis of arrangement of the elements is their atomic numbers.

Each element has a serial number called its **atomic number**. Atomic numbers start with hydrogen = 1 and end with uranium = 92. In Table XX the elements are arranged in the same general way as in the old periodic arrangement, but this time in the strict order of their atomic numbers. Several points should be noted.

(1) The general arrangement into groups and periods is unchanged.

TABLE XX. — ARRANGEMENT OF THE ELEMENTS BY ATOMIC NUMBERS

PERIOD	GROUP 0	GROUP I	GROUP II	GROUP III	GROUP IV	GROUP V	GROUP VI	GROUP VII	GROUP VIII
1	2 Helium ¹	3 Lithium	4 Beryllium	5 Boron	6 Carbon	7 Nitrogen	8 Oxygen	9 Fluorine	
2	10 Neon	11 Sodium	12 Magnesium	13 Aluminum	14 Silicon	15 Phosphorus	16 Sulphur	17 Chlorine	
3	18 Argon	19 Potassium	20 Calcium	21 Scandium	22 Titanium	23 Vanadium	24 Chromium	25 Manganese	26 Iron
		29 Copper	30 Zinc	31 Gallium	32 Germanium	33 Arsenic	34 Selenium	35 Bromine	27 Cobalt
4	36 Krypton	37 Rubidium	38 Strontium	39 Yttrium	40 Zirconium	41 Columbium	42 Molybdenum	43 Massium	28 Nickel
		47 Silver	48 Cadmium	49 Indium	50 Tin	51 Antimony	52 Tellurium	53 Iodine	44 Ruthenium
5	54 Xenon	55 Cæsium	56 Barium	57 Lanthanum	58 Cerium ²	73 Tantalum	74 Tungsten	75 Rhenium	45 Rhodium
		79 Gold	80 Mercury	81 Thallium	82 Lead	83 Bismuth	84 (Polonium)	85 —	46 Palladium
6	86 Radon	87 —	88 Radium	89 (Actinium)	90 Thorium	91 —	92 Uranium		76 Osmium
									77 Iridium
									78 Platinum

¹ Hydrogen (1) has no tabular position.² Elements between Cerium and Tantalum are 59 Praseodymium, 60 Neodymium, 61 Illinium, 62 Samarium, 63 Europium, 64 Gadolinium, 65 Terbium, 66 Dysprosium, 67 Holmium, 68 Erbium, 69 Thulium, 70 Ytterbium, 71 Lutecium, 72 Hafnium (Celtium).

(2) All the elements are in their proper places. That is, the three pairs of elements, anomalously located by their atomic weights, are now in the correct order. Specifically, (a) argon, atomic number 18, precedes potassium, atomic number 19, (b) cobalt (27) precedes nickel (28), and (c) tellurium (52) precedes iodine (53).

(3) The rare earth elements (see footnote 2 in Table XX) which have atomic numbers 59 to 72 are omitted from the table to avoid confusion.

(4) Hydrogen (atomic number = 1) has no acceptable place.

424. Determination of the atomic number of an element.—The atomic numbers of the elements are assigned from the relative value of their X-ray spectra.

Light and X-rays are similar. Both affect a photographic plate. The essential difference is in the wave lengths, X-ray waves being very much shorter.

Visible light in passing through a glass prism is spread out into a band of colors called a **spectrum**. A spectrum is also produced by letting light fall upon a diffraction grating, *i.e.*, a plane surface of glass or metal on which is ruled an enormous number of fine parallel lines, the lines being separated by distances of the order of the wave length of light.

Diffraction gratings cannot be ruled fine enough for X-ray spectra. But crystals can be used to produce X-ray spectra, because the atoms in crystals are arranged in successive rows and layers so close together that they actually form a grating of the fineness adapted to X-rays.

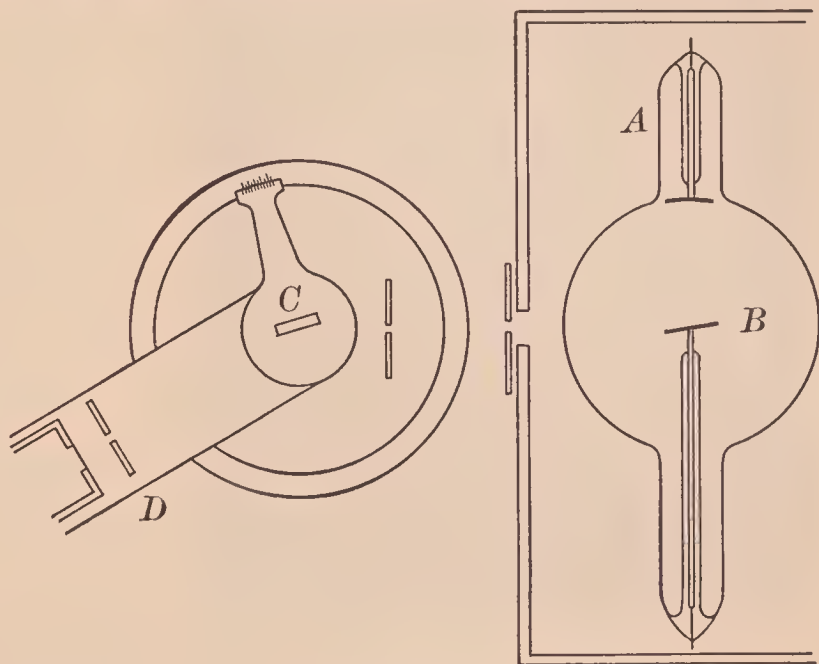


FIG. 187. — Sketch of the apparatus for finding X-ray spectra.

When a high-voltage electric current is passed through a vacuum tube *A* (Fig. 187), rays called cathode rays (*i.e.*, a stream of negatively charged particles of electricity called electrons) are given off at the cathode. If the cathode rays strike a solid, metallic target *B* (called the anti-cathode), part of their energy is transformed into X-rays, which emerge from the tube. These X-rays, in passing through a slit and falling upon the crystal *C*, produce the



FIG. 188. — The English physicist Moseley (1889–1915), whose studies of X-ray spectra led to the atomic numbers of the elements.

X-ray spectra (alluded to above), which may be photographed on a plate mounted beyond *D*. A given element yields a characteristic X-ray spectrum.

The facts, substantially as just stated, were discovered and first utilized by the gifted young English physicist Moseley (Fig. 188).

Moseley found by experiment that the X-ray spectra of different metals have conspicuous lines. And he discovered that there is a regular change in the position of the lines as one metal after another is used in the order of their increasing atomic weights. By assigning a number to a given element, *e.g.*, aluminum = 13, he found he could arrange the elements he examined in a series which increased numerically by 1 as he passed up the series. Furthermore, he found that the order is the same as that required in the old periodic classification — no exceptions in the new order.

Moseley's work has been extended, and now each element is assigned a number, according to its position in the series,

thereby giving a succession of whole numbers from 1 (for hydrogen) to 92 (for uranium). These numbers are the **atomic numbers**. They are numerically equal to the number of electrons surrounding the nucleus of the atom.

425. The new periodic table and law. — The new table (XX) of the elements arranged according to their atomic numbers is almost exactly like the old one based on atomic weights. The only apparent difference is that all the elements are now in their correct periodic places, that is, in the correct groups, *e.g.*, argon in group 0 and potassium in group I.

The atomic number of an element is more fundamental than its atomic weight. Many experiments have convinced chemists that atomic numbers are a deep and comprehensive expression of the properties of elements. Hence the relations expressed in the new periodic table can be summarized in the **new periodic law** thus: —

The properties of the elements are a periodic function of their atomic numbers.

EXERCISES

1. What is meant by (a) period, (b) group, (c) family?
2. Illustrate the periodic arrangement by periods 1 and 2.
3. Commit to memory the names of the elements in Groups 0, I, II, VII.
4. As in Exercise 2 by the proper elements in groups I and VII.
5. What is the atomic number of an element?
6. What is the atomic number of hydrogen, oxygen, carbon, nitrogen, chlorine, iron, calcium, sodium?

PROBLEMS (Review)

1. Calculate the per cent of oxygen in (a) water, (b) potassium chlorate, (c) nitric acid, (d) lime.
2. A candle in burning forms 13.21 gm. of carbon dioxide and 5.58 gm. of water. How much weight did the candle lose? What volume of oxygen at 0° C. and 760 mm. was required?
3. What volume of air (free from carbon dioxide and water vapor) contains 1 gm. of nitrogen?
4. What weight of sulphur is contained in 500 cc. of SO₂?

5. Suppose 50 l. of nitrous oxide are decomposed into nitrogen and oxygen. How many volumes of the products are formed?

6. A compound has the composition C = 10.04, H = 0.836, Cl = 89.13, and the vapor density is 3.735. What is the molecular formula?

TOPIC XX: FLUORINE — BROMINE — IODINE

426. The halogen family. — Fluorine, bromine, and iodine, together with chlorine (§§ 120–137), constitute a typical

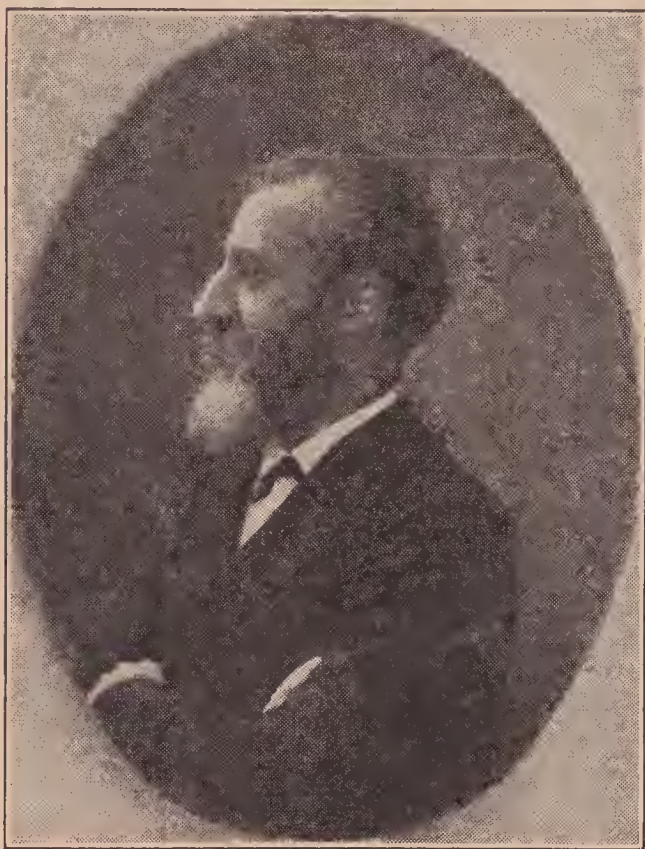


FIG. 189. — The French chemist Moissan (1852–1907), who first prepared the corrosive element fluorine.

family of related elements often called the **halogens**. The elements and their analogous compounds have similar properties, differing mainly in degree (§ 440).

FLUORINE

427. Occurrence of fluorine. — Fluorine occurs only in combination with other elements, *e.g.*, with calcium as calcium fluoride (fluor spar, fluorite, CaF_2). Other native compounds are cryolite (Na_3AlF_6) and apatite ($\text{Ca}_5\text{F}(\text{PO}_4)_3$).

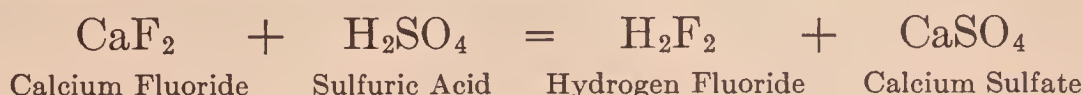
428. Preparation of fluorine. — Fluorine was first isolated in 1886 by the French chemist Moissan (Fig. 189) by the electrolysis of a mixture of anhydrous hydrofluoric acid (H_2F_2) and acid potassium fluoride (KHF_2). The experiment was difficult and dangerous owing to the corrosive properties of both acid and element.

Fluorine can be prepared on a commercial scale by the electrolysis of molten acid potassium fluoride (KHF_2) in a graphite cell, which serves as the cathode. The anode is a graphite rod. It passes down through

a graphite cylinder (in which the fluorine collects) which dips just below the surface of the molten fluoride.

429. Properties of fluorine. — Fluorine is a greenish yellow gas. It smells like chlorine. Chemically, fluorine is intensely active. It combines with most elements readily, the combining being accompanied by much heat and light. The compounds formed are fluorides. It does not combine with oxygen or nitrogen; while some metals, *e.g.*, gold, platinum, and copper, are not readily (or only slightly) attacked by it. Water is decomposed by it at ordinary temperature.

430. Hydrogen fluoride. — This gas is prepared by the interaction of concentrated sulfuric acid and calcium fluoride. The experiment is performed in a lead dish because hydrogen fluoride is so corrosive. The equation is: —

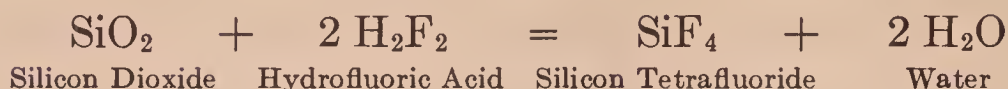
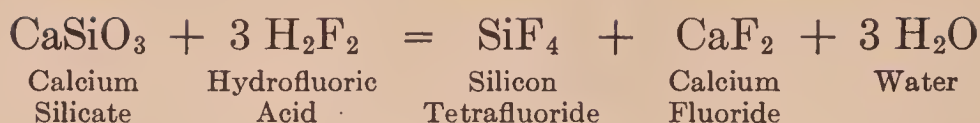


Hydrogen fluoride forms fumes in moist air and dissolves readily in water. (Compare § 131.) The solution is **hydrofluoric acid**. The gas and solution are dangerous substances. The gas is poisonous, and the acid if dropped on the skin produces terrible sores. Owing to its corrosive properties, hydrofluoric acid is kept in wax or bakelite bottles.

Bakelite is a resinous substance, which resists the action of many chemicals, being practically inert. It has numerous applications, particularly in electrical apparatus.

Hydrofluoric acid behaves chemically much like hydrochloric acid. It is unlike hydrochloric acid in one respect; it forms both normal and acid salts, *e.g.*, potassium fluoride (K_2F_2) and acid potassium fluoride (KHF_2).

431. Etching with hydrofluoric acid. — The acid and moist gas attack glass, and are used extensively in **etching**. Glass is essentially a mixture of silicates and silica (§§ 449, 450). Hydrofluoric acid interacts with these compounds and forms among other substances the volatile compound called silicon tetrafluoride (SiF_4). Hence the acid disintegrates the glass — literally “eats” or etches it. Typical equations for the reactions are: —



In **etching with hydrofluoric acid**, the glass is thinly coated with wax, and the design or marks to be etched are scratched through the wax. The glass is then exposed to the gas or liquid, which attacks the unprotected places. When the wax is removed, a permanent etching is left. Hydrofluoric acid is used in marking the scales on thermometers, tubes, and other graduated glass instruments, and also in etching designs on glassware (Fig. 190).



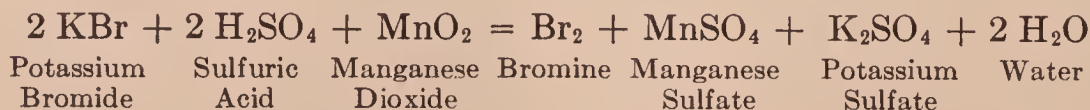
FIG. 190.—Etching on glass tumbler. (Designed and executed by a high school pupil.)

BROMINE

432. Occurrence and preparation of bromine.—Bromine is never found free, but bromides are widely distributed, especially magnesium and sodium bromides. The salt springs and wells of Ohio, West Virginia, Pennsylvania, and

Michigan contain bromides. Large quantities are found in the salt deposits at Stassfurt in Germany.

Bromine is **prepared in the laboratory** by heating a bromide with manganese dioxide and sulfuric acid (Fig. 191), thus:—



Another method consists in warming a bromide solution with chlorine; an equation for this method is:—

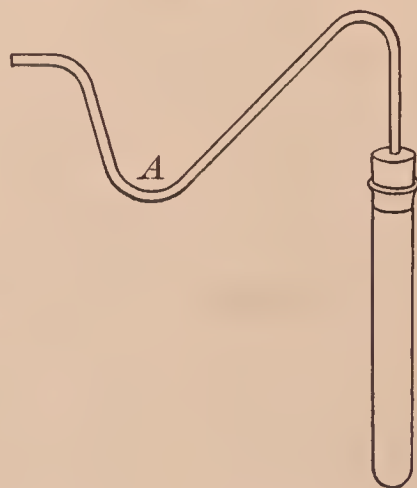
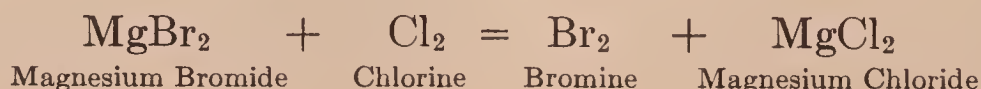


FIG. 191.—Apparatus for preparing bromine in the laboratory.

The chlorine method is used to **manufacture bromine** from the concentrated solution of bromides (largely magnesium bromide) called **bittern**, which is left after sodium chloride has been removed by crystallization from the brine of salt wells.

A sketch of the apparatus is shown in Figure 192. The bromide solution enters the tank at *B*, falls as a spray upon the resistant material, trickles down, and meets the ascending chlorine (gas) which is forced in at *A*. The liberated bromine escapes as a vapor through *C*, and the magnesium chloride flows out through *D*. In this process, chlorine, being the more active element, displaces bromine, thus,



433. Properties of bromine. — Bromine is a dark red liquid which is about three times as heavy as water. It is a volatile liquid, boiling at 59°C . The vapor, which has a disagreeable odor, irritates the mucous membrane of the eyes, nose, and throat. A bottle of bromine should not be opened unless it is in the hood.

Bromine is moderately soluble in water. The solution is called **bromine water**. Bromine dissolves in carbon disulfide and carbon tetrachloride; the solution is reddish yellow. Liquid bromine burns the flesh frightfully, and care should be used in preparing it or working with it.

The chemical behavior of bromine is similar to that of chlorine, though bromine is less active. It combines with metals, *e.g.*, magnesium and iron.

434. Compounds of bromine. — These are similar to those of chlorine. **Hydrogen bromide** (HBr) is a colorless, pungent gas, which fumes in the air and dissolves freely in water.

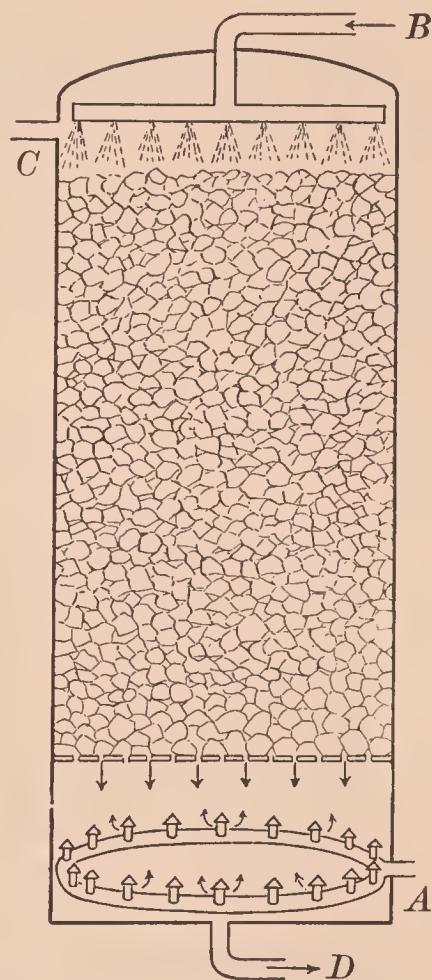


FIG. 192. — Sketch of the apparatus for manufacturing bromine.

This solution is called **hydrobromic acid**; it is much like hydrochloric acid. **Bromides** are salts of hydrobromic acid. **Potassium bromide** (KBr) is a white solid, made by decomposing iron bromide with potassium carbonate; it is used as a medicine. **Silver bromide** (AgBr) is a pale yellow solid, and is used extensively in making photographic films and plates.

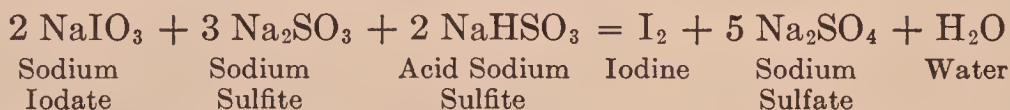
IODINE

435. Occurrence of iodine. — Iodine, like fluorine, chlorine, and bromine, is found in nature only in compounds. Tobacco, water cress, cod-liver oil, oysters, and marine plants contain minute quantities. Sea water contains a very small proportion of iodine compounds, which are assimilated by seaweeds. Iodine was formerly extracted from the ash of certain seaweeds.

Iodine compounds, chiefly sodium iodate (NaIO_3), occur in the deposits of sodium nitrate in Chile, and most of the iodine of commerce is obtained from this source.

436. Preparation of iodine. — Iodine is prepared in the laboratory by the same method as that used for bromine; potassium iodide is used instead of potassium bromide.

Iodine is **manufactured** from sodium iodate which is left in the Chile sodium nitrate residues. The equation is: —



437. Properties of iodine. — Iodine is a lustrous, gray-black crystalline solid. When gently heated, it changes into a beautiful violet-colored vapor, which quickly solidifies on a cold surface. This property of iodine, *viz.*, ready transformation from solid into vapor and back directly into solid, is utilized in purifying iodine. The crude substance is heated gently and the vapor condensed; the non-volatile impurities remain behind. This process is called **sublimation** and is frequently used to purify substances, *e.g.*, ammonium chloride (§ 196).

Iodine dissolves slightly in water but freely in alcohol, chloroform, carbon disulfide, ether, carbon tetrachloride,

and potassium iodide solution. The chloroform and carbon disulfide solutions are violet, but the others are brown, or even black. Iodine and its solutions turn the skin brown.

Iodine turns a cold starch suspension blue. The presence of starch in many vegetable substances can thus be readily shown (§ 261). A minute trace of iodine may be detected by starch, and this experiment also serves as a **test for iodine**. The colloidal starch adsorbs the iodine.

In chemical properties iodine resembles chlorine and bromine, but iodine is less active. Bromine and chlorine displace iodine from many of its compounds.

438. Uses of iodine. — A solution of iodine in alcohol (or in alcohol and potassium iodide), called tincture of iodine, or merely “iodine,” is applied to the skin to harden it, to prevent the spread of eruptions, or to reduce swellings. Iodine is used to make iodoform (CHI_3), which is an anti-septic for wounds. Large quantities of iodine are made into iodides, drugs, and dyes.

439. Compounds of iodine. — These are similar to the corresponding compounds of chlorine and bromine. **Iodides** are salts of hydriodic acid (HI). The best known salt is **potassium iodide** (KI). **Silver iodide** (AgI), like silver bromide, is used in photography (§ 491).

440. The halogen elements and the periodic classification. — The halogen elements illustrate the periodic classification (§§ 418–421). These elements, as arranged in the periodic table, increase in atomic weight from fluorine through chlorine and bromine to iodine, and many of their properties are graded in this order. Thus, as we pass from fluorine to iodine the specific gravity increases, the color grows deeper, the volatility decreases, and the melting points of the solidified elements increase. The intensity of the chemical action decreases as we pass from fluorine to iodine.

EXERCISES

1. Summarize the chief properties of fluorine and hydrogen fluoride.
2. Describe the process of etching glass. Write the equations.
3. Write the equations for the preparation of (a) hydrogen fluoride, (b) bromine, (c) iodine, (d) silver bromide. Write (d) in ionic form.

4. Write the formulas of the fluoride, bromide, and iodide of Al, ammonium, Ba, Ca, copper (ous and ic), Fe^{+2} , Fe^{+3} , Pb^{+2} , magnesium, Sb^{+3} , Si, Hg (ous and ic), Sn^{+2} , Sn^{+4} , zinc.

PROBLEMS

1. Calculate the per cent of bromine or iodine in (a) sodium bromide, (b) hydrogen bromide, (c) calcium iodide, (d) sodium iodate.

2. How much (a) calcium sulfate and (b) hydrogen fluoride are formed by heating 60 gm. of fluor spar with sulfuric acid?

3. How much potassium bromide (95 per cent pure) is necessary to prepare 47 gm. of bromine?

4. Calculate the atomic weight of fluorine, bromine, or iodine from the following: (a) 1 gm. of CaF_2 gives 1.745 gm. of CaSO_4 ; (b) 3.946 gm. of Ag (dissolved in HNO_3) require 4.353 gm. of KBr for precipitation; (c) 6.3835 gm. of silver iodide give 3.8965 gm. of silver chloride.

5. Calculate the simple formulas corresponding to (a) $\text{F} = 48.72$, $\text{Ca} = 51.28$; (b) $\text{Br} = 67.22$, $\text{K} = 32.77$; (c) $\text{I} = 76.5$, $\text{K} = 23.49$.

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

Exercise	S44 — Preparation and Properties of Bromine — T.
Exercise	S45 — Bromine (Short Method).
Exercise	S46 — Tests for Free and Combined Bromine.
Exercise	S59 — Testing Salts (Bromide part only).
Exercise	S60 (e) — Silver Salts and Photography — T.
Exercise	S47 — Preparation and Properties of Iodine — T.
Exercise	S48 — Iodine (Short Method).
Exercise	S49 — Tests for Free Iodine.
Exercise	S50 — Tests for Combined Iodine.
Exercise 55	(c), (d) — Tests for Starch.
Exercise	S59 — Testing Salts (Iodide part only).

TOPIC XXI: SILICON DIOXIDE — SILICATES — SILICON CARBIDE — SILICON TETRAFLUORIDE — GLASS

441. Occurrence of silicon dioxide. — The most abundant and important compound of silicon is **silicon dioxide** (SiO_2). It is often called **silica**. Sand, gravel, sandstone, and the numerous varieties of quartz are almost wholly silicon dioxide; many rocks, *e.g.*, granite and gneiss, contain silica as an essential ingredient. Ordinary soil contains more or less silica.

Quartz is the commonest form of silicon dioxide. Pure quartz is colorless and transparent, and is called rock crystal. There are many colored varieties, which are used as semi-precious jewels, *e.g.*, amethyst, onyx, carnelian. It is crystalline and is found in groups or as single crystals (Fig. 193).

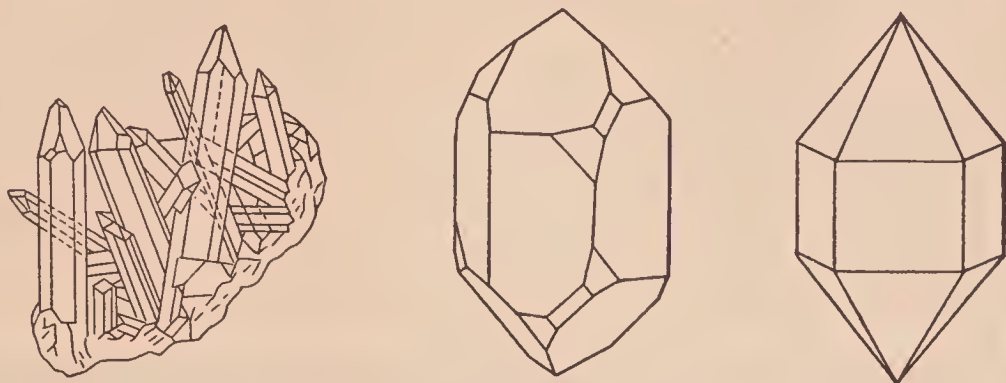


FIG. 193. — Quartz crystals—group (left), single crystals (center and right).

Petrified or silicified wood is the remnant of wood in which the fiber has been replaced by silica. There is a forest of petrified trees in Arizona. Infusorial or diatomaceous earth (also called Tripoli powder) is largely silica and consists of the skeletons of minute organisms called diatoms, many being of delicate and beautiful structure (Fig. 194).

442. Properties of silicon dioxide. — Most varieties of silicon dioxide are hard and brittle. Quartz is harder than other common substances, and it breaks into fragments with sharp edges.

Quartz melts at about 1600°C . and can be melted only in



FIG. 194. — Diatom shells (enlarged).

the oxy-hydrogen flame or the electric furnace. If pure silica is fused with certain precautions, the viscous mass can be drawn into elastic threads, which are used to suspend delicate parts of electric instruments; it can also be shaped into tubes, flasks, crucibles (Fig. 195), and even large pieces of apparatus used in industrial processes, *e.g.*, dishes for crystallizing corrosive solutions and tubes for condensing acid vapors.

By melting fragments of quartz (rock crystal) in an electric

furnace, first under reduced and finally under increased pressure, transparent quartz can be produced as rods, sheets, disks, lenses, and other forms, which are used in moving picture projection, photography, astronomy, and microscopy (Fig. 196).

Objects made of fused quartz expand or contract only a very little within a wide range of temperature, *i.e.*, they have a low coefficient of expansion, being only about 0.00000449 between 0° C. and 1000° C. Thus, a silica crucible, unlike a porcelain one, will not crack if heated and then plunged at once into cold water. Similarly, the quartz lenses, which have largely replaced the glass condensing lenses in moving

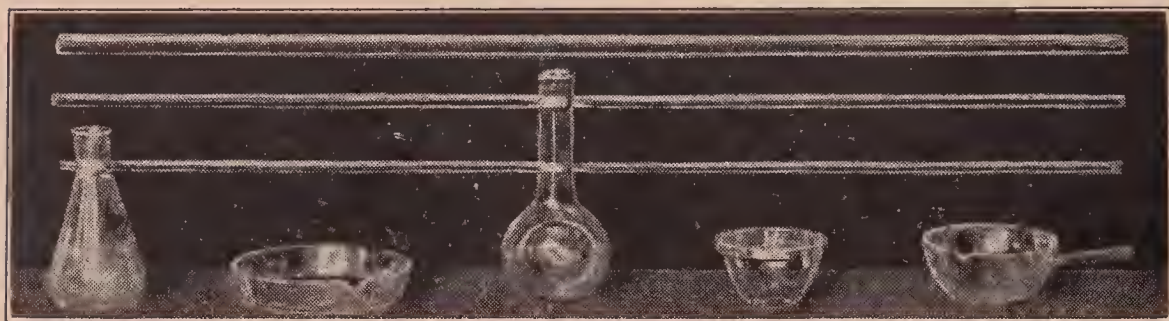
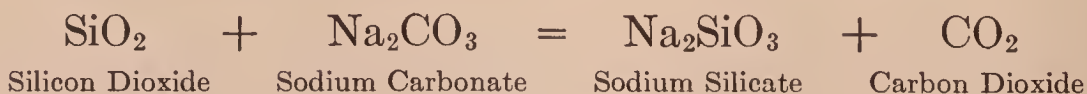


FIG. 195. — Apparatus made from fused silica for use in the laboratory.

picture projection machines, do not crack even at the high temperature of the electric arc.

Silicon dioxide does not dissolve in water. Nor is it attacked by acids, except hydrofluoric acid (§§ 430, 431). It is converted into a soluble silicate when boiled in water containing alkaline substances or when fused with the hydroxides or the carbonates of sodium and potassium, thus:—



443. Uses of silicon dioxide.— Sandstone is used as a building stone, and some varieties of sandstone are shaped into grindstones and whetstones. Large quantities of sand are used to make glass, porcelain, cement, and mortar. Different grades of sand are used as grinding and polishing material. Glass is polished by rubbing it with fine wet sand; it is also roughened and cut by blowing or “blasting” fine

sand against it. Glass stoppers for bottles used in the laboratory are "ground" with sand.

Infusorial earth (Fig. 194) is used as a polishing powder for metals ("electro-silicon" being the commercial name of one kind), and in making scouring soaps. Owing to the hollow structure of its minute particles, considerable is used as an absorbent of nitro-glycerin in the manufacture of dynamite.

444. Silicates. —

These are salts of silicic acids. Only two silicic acids are well known, *viz.*, metasilicic acid (H_2SiO_3) and orthosilicic acid (H_4SiO_4). The salts of these and other silicic acids (not yet prepared) are among the most common substances in the earth's crust.

Most rocks consist wholly or largely of silicates of the metals aluminum, iron, calcium, potassium, sodium, and magnesium. Examples of silicates are slate, asbestos ($\text{Mg}_3\text{Ca}(\text{SiO}_3)_4$), feldspar (KAlSi_3O_8), mica, hornblende, clay ($\text{H}_2\text{Al}_2(\text{SiO}_4)_2 \cdot \text{H}_2\text{O}$), beryl, garnet, serpentine ($\text{Mg}_3\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$), and talc ($\text{H}_2\text{Mg}_3(\text{SiO}_3)_4$). The lava ejected by volcanoes consists largely of fused silicates.

445. Sodium silicate. — When fine sand and sodium carbonate are fused together, sodium (meta-) silicate (Na_2SiO_3) is formed (see § 442 end). Sodium silicate is a glassy solid, which dissolves in water; hence this silicate is sometimes called **water glass**. Silicate of soda is the name given to commercial solutions of varying composition, which also contain some silica in the colloidal state (§§ 95, 446).

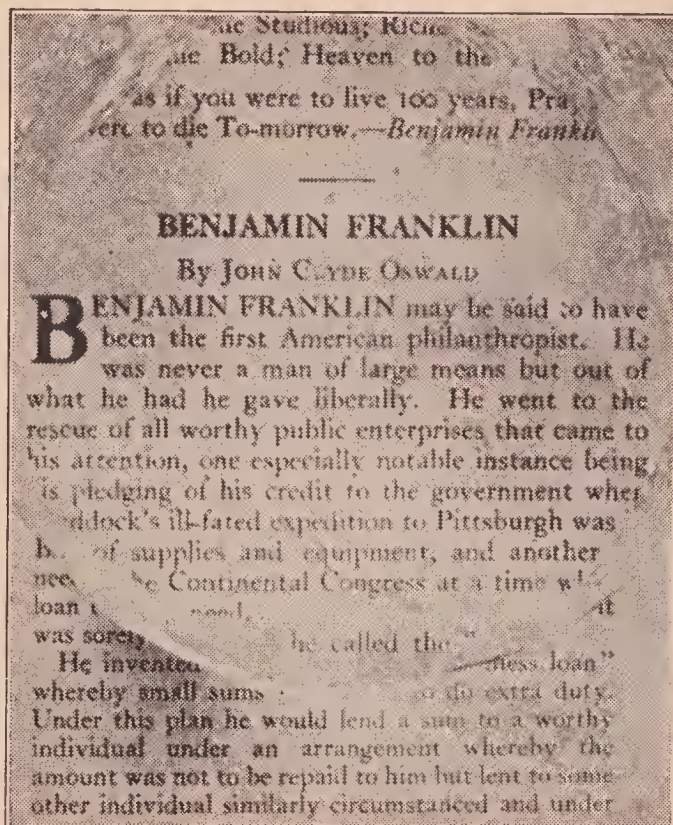


FIG. 196. — Photograph of a printed page made through disks of transparent quartz nine inches thick.

Solutions of sodium silicate have different properties adapted to special uses. Certain brands are used as the adhesive in making corrugated paper board, fiber board, and wall board. Paper board and fiber board are made into cartons, tubes, trunks, and containers of various kinds (Fig. 197). Wall board is used as a substitute for wood. Another brand of silicate of soda is used as a binder in abrasive wheels, stove and furnace cements, and linings. Still another use is as a protective coating for wood, paper,

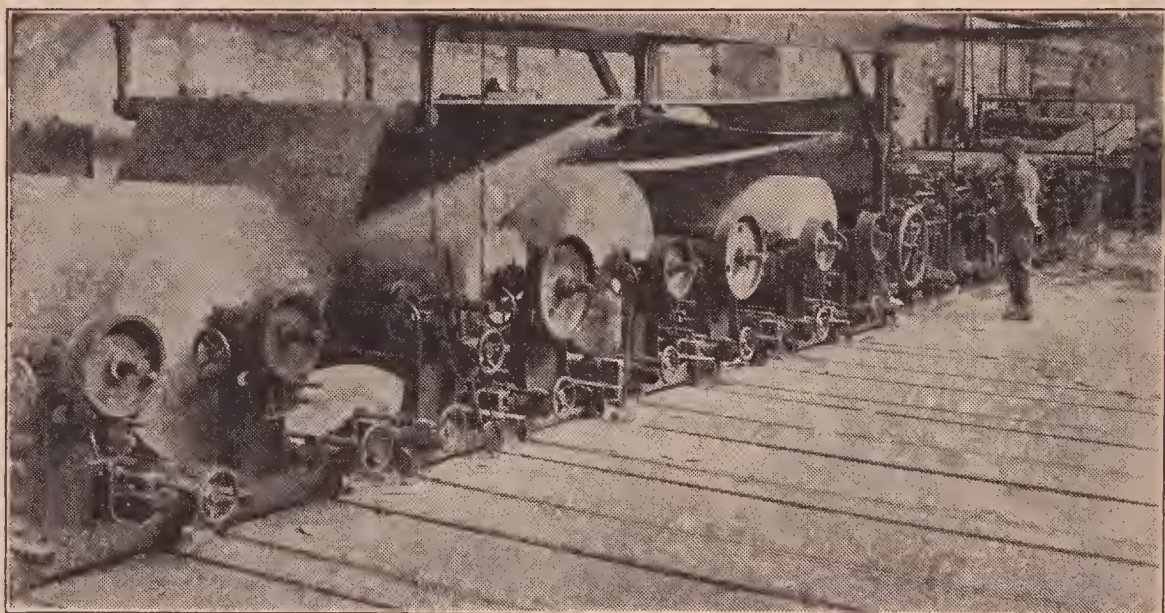
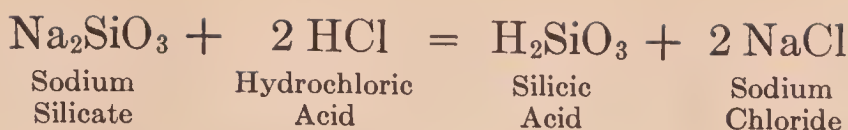


FIG. 197. — Making 4-ply paper board used for cartons, shipping containers, and wall board. The two center strips are coated on both sides with sodium silicate solution; the upper and lower strips on one side only. All four strips are united firmly together by pressure rolls. This machine is one of the largest in use and turns out over 200 feet of finished board per minute.

and concrete, a fireproof coating or ingredient of wood and fabrics, and a preservative coating for eggs. The last use is based on the fact that the deposit of silica in the pores of the shells keeps out the air and thus prevents the eggs from spoiling. Finally, considerable is used in many chemical processes, *e.g.*, the manufacture of certain laundry soaps, sizing of paper, refining of oil, and removing paint.

446. Colloidal silicic acid. — When hydrochloric acid is added to sodium silicate solution, a white gelatinous precipitate called silicic acid is formed, thus : —



Under certain conditions probably the precipitate is a mixture of meta- and ortho-silicic acids (H_2SiO_3 and H_4SiO_4). These acids are closely related. The ortho-acid passes into the meta-acid upon drying, thus: —



And metasilicic acid when heated decomposes into silicon dioxide and water, thus: —



Silicon dioxide may be regarded as the anhydride of metasilicic acid, though contrary to the usual rule this acid can not be formed from the anhydride (SiO_2) and water (§§ 85, 219).

Sodium silicate and hydrochloric acid do not always interact as just described. That is, the silicic acid is not gelatinous, but is dispersed throughout the liquid in the colloidal state (§ 95). This **colloidal silicic acid** can not be filtered out because the colloidal particles are so fine they pass through the paper. It can be separated by **dialysis** from the sodium chloride in the solution. Thus, if the colloidal suspension of silicic acid is placed in a vessel, which has a bottom of parchment, and hung in a larger receptacle filled with water, the sodium chloride will pass through the parchment into the water, but the silicic acid will be retained in the smaller vessel.

The gelatinous silicic acid is an example of a hydrogel, or, more frequently called, a gel. Whereas the colloiddally suspended silicic acid is an example of a hydrosol, or simply a sol.

447. Silicon carbide or carborundum. — This is a crystallized solid, which varies in color from white to green or black. It is extremely hard, being nearly as hard as diamond. It is very resistant to chemicals. The extreme hardness of

carborundum has led to its extensive application as an abrasive, and large quantities are made into a great variety of grinding wheels, whetstones, and polishing cloths (Fig. 18).

Carborundum is manufactured by fusing a mixture of sand (silicon dioxide, SiO_2) and coke (carbon, C) in an electric furnace similar in form to that used in the manufacture of graphite (Fig. 198). The mixture of sand and coke (to which salt and sawdust are added to contribute to the fusion and porosity) is packed around the core of granulated coke. The heat generated by the resistance of the carbon core to the passage

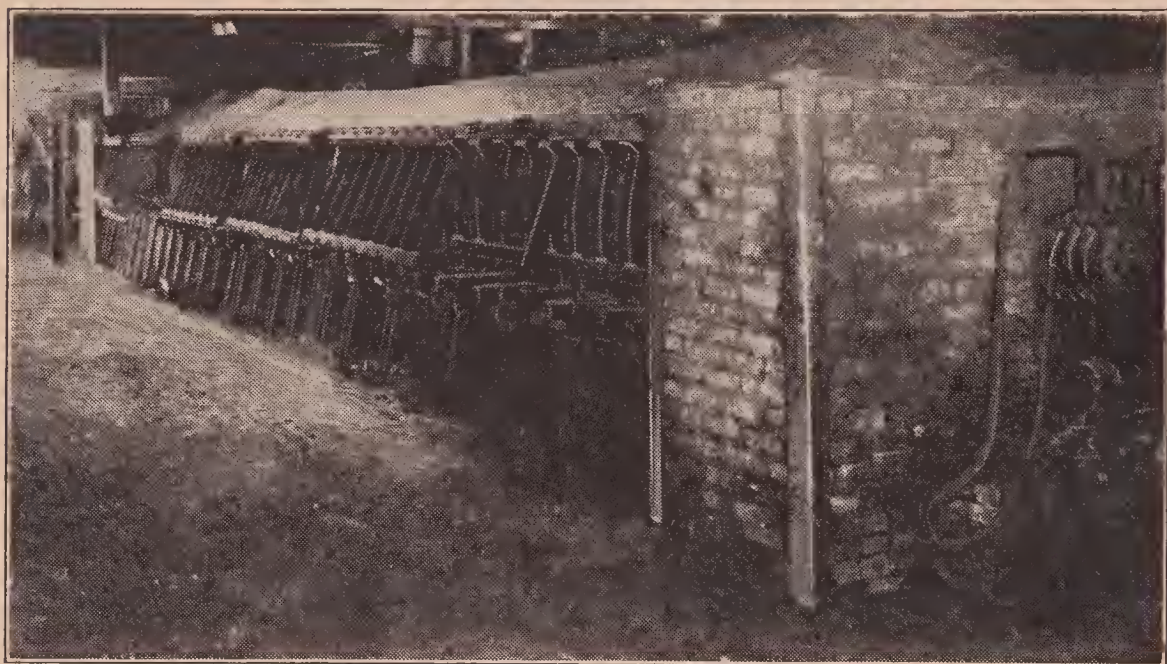
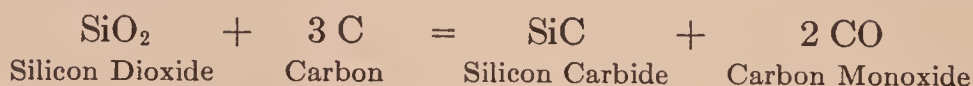
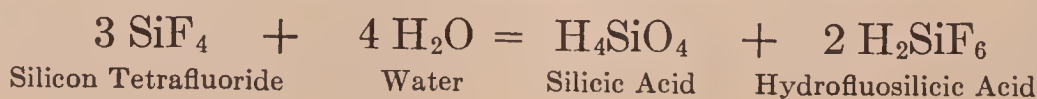


FIG. 198. — Furnace for the manufacture of carborundum.

of the powerful current of electricity produces a chemical change essentially as follows:—



448. Silicon tetrafluoride. — When hydrofluoric acid interacts with silicon dioxide, silicates, or silicon, silicon tetrafluoride (SiF_4) is formed (§ 431). Silicon tetrafluoride is a colorless, volatile liquid. In the World War it was used to produce a smoke screen, because with ammonia and water it forms a dense white smoke consisting of silicic acid and ammonium chloride (Fig. 56). It fumes in moist air owing to interaction with water. The equation for the reaction is:—



The hydrofluosilicic acid (sometimes called fluosilicic acid) remains in solution, while the (ortho) silicic acid is precipitated. The formation of the white gelatinous silicic acid when the gases from the interaction of hydrofluoric acid and a compound of silicon are led into water is often used as a **test for silicon**.

449. Glass. — This substance is essentially a mixture of silicates and silica. Ordinary glass, such as that used for bottles, is made by heating sand, calcium carbonate, and sodium carbonate to a high temperature. The product is a mixture of calcium silicate (CaSiO_3), sodium silicate (Na_2SiO_3), and silica (SiO_2). Sodium-calcium glass is called **soft glass** because it softens readily when heated.

Other varieties can be made by substituting other substances, wholly or partly, for the calcium and sodium compounds. Thus, potassium carbonate (with calcium carbonate) produces a **hard glass**, which melts at a higher temperature than sodium glass.

If a lead compound is used in place of calcium carbonate, **flint glass** is produced which refracts light to a high degree; it is used to make lenses for optical instruments, and shades for gas and electric lights. On account of its brilliancy this glass is made into cut glass vessels for ornaments and table use.

Another kind of glass, used extensively for chemical apparatus and certain cooking utensils, contains a large excess of silica together with boron oxide (B_2O_3) and aluminum oxide (Al_2O_3). It is made by heating together sand, borax ($\text{Na}_2\text{B}_4\text{O}_7$), and aluminum oxide. This glass is tough and has a much lower coefficient of expansion than ordinary glass; hence it does not crack with sudden changes of temperature. It is called **pyrex glass**.

450. Manufacture of glass. — The ingredients needed for the different varieties of glass are mixed in the proper proportions and heated to a high temperature in a long tank, or in large clay vessels. The substances interact and form a heavy, viscous, semi-fluid mass, which can be poured into molds, rolled into sheets, and fashioned into various shapes by blowing, pulling, pressing, or stamping.

Bottles, jars, and electric light bulbs are manufactured by complicated machines. Special or ornamental objects are blown into a mold. A

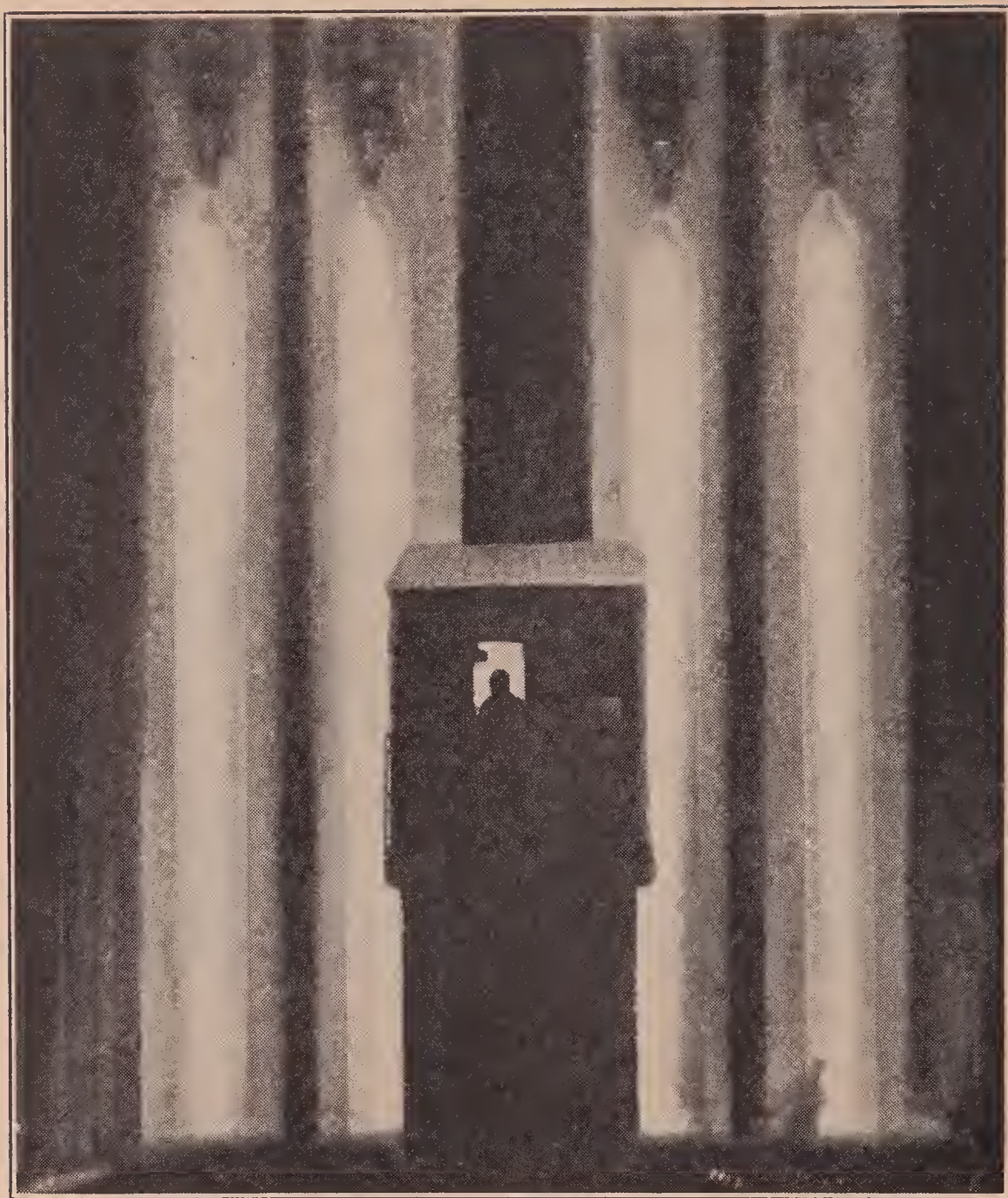


FIG. 199. — Blowing huge cylinders of glass by compressed air. These are slit open and allowed to roll out flat.

skilled workman gathers a mass of the plastic glass on the end of a long tube, called a glass blowpipe, blows the glass into a preliminary shape, lowers it into a mold, and blows until the mold is filled.

Window glass and other kinds of flat glass are made by machinery. (1) In one process the glass is blown by compressed air into a long cylinder (Fig. 199) which is allowed to cool; the ends are then cut off, the cylinder is slit lengthwise, heated until it softens and opens, and then allowed to roll out flat. (2) In another process the mixture of the raw materials is put into a furnace, melted, and transformed into

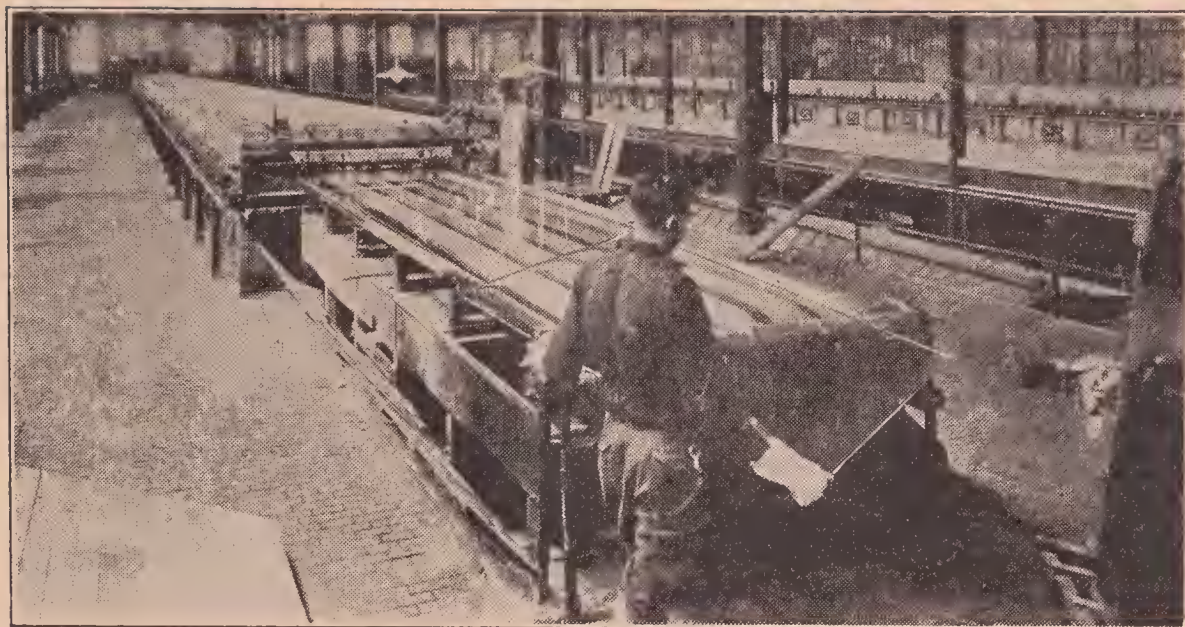


FIG. 200. — Removing a sheet of glass from an automatic sheet glass machine. The raw materials enter at one end and the sheets of glass are cut off at the other.

glass. The viscous mass is moved along (in the same machine) to a bar which sticks to it, pulls it forward between rolls, through a cooling chamber, and finally out upon a table where the flat glass is automatically cut into sheets. In Fig. 200 a workman is shown taking off a sheet of glass.

Plate glass, which is used for windows and wind shields, is made by the flat process or by pouring the molten glass into a shallow frame upon a large table, rolling it with a hot steel roller, as if it were dough, and

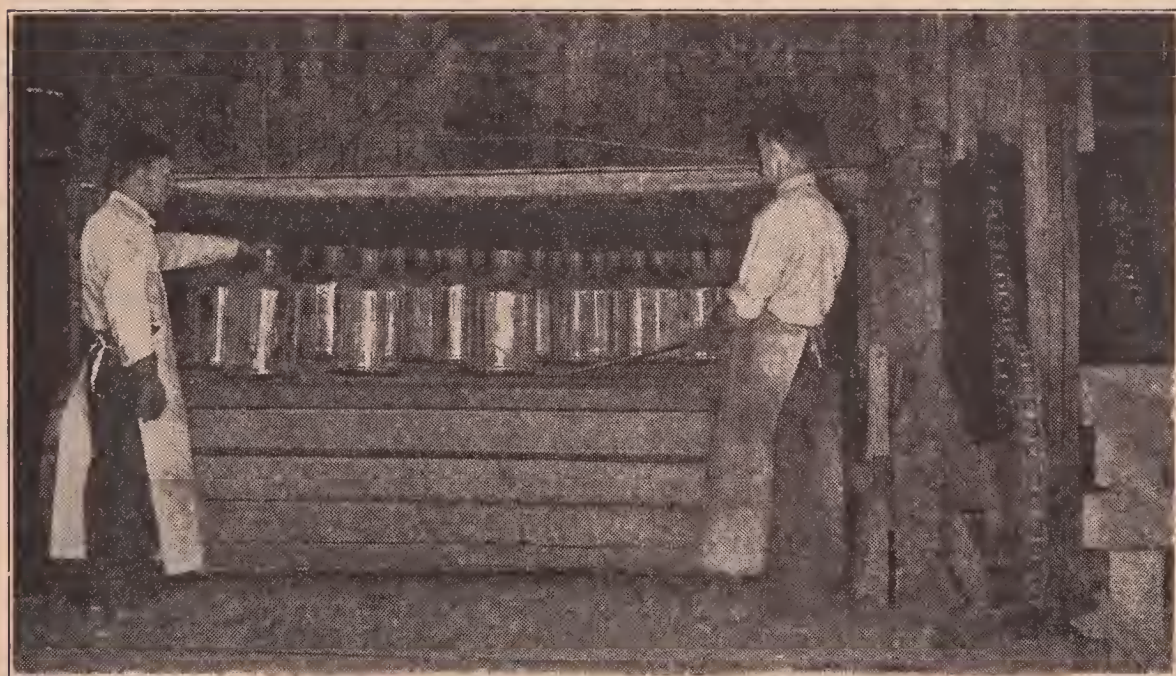


FIG. 201. — Bottles just coming from an annealing chamber which is called a lehr.

finally grinding and polishing the cooled sheet on a rotating table until the surfaces are parallel.

Glass must be cooled slowly, otherwise it will crack or crumble to pieces when jarred or scratched. This slow cooling is called **annealing**. It is accomplished by passing the objects on a slowly moving frame through a long chamber in which the temperature is gradually lowered (Fig. 201).

EXERCISES

1. Summarize the properties of silica.
2. Describe the formation, state the uses, and enumerate the properties of water glass.

PROBLEMS

1. Calculate the per cent of silicon in (a) orthosilicic acid, (b) metasilicic acid, (c) potassium feldspar (KAlSi_3O_8).
2. How much sodium silicate can be made from 1000 kg. of sand?
3. Calculate the simplest formulas corresponding to (a) $\text{Si} = 35.897$, $\text{H} = 2.564$, $\text{O} = 61.538$; (b) $\text{Si} = 29.166$, $\text{H} = 4.166$, $\text{O} = 66.666$.

TOPIC XXII: COPPER

451. History. — Copper has been known for ages. Domestic utensils and weapons of war containing copper were used before similar objects of iron. The Latin word *cuprum* gives the symbol Cu.

452. Copper ores. — Free or native copper, mixed with a hard rock, is found in large quantities in the Michigan mines on the shore of Lake Superior. The most abundant copper ores are the copper-iron sulfide ores, *e.g.*, chalcopyrite (CuFeS_2), and bornite (Cu_3FeS_3), found in Montana and Utah (Fig. 202).

453. Metallurgy of copper. — Free copper is easily extracted. The ore is crushed, concentrated by grinding and then washing away the rocky impurities down an inclined plane or on shaking tables, and finally heated (*i.e.*, smelted) with a flux.

The metallurgy of the copper-iron sulfide ores is complicated. It involves the removal of sulfur and iron. The result is accomplished by converting the sulfur into sulfur

dioxide, which escapes as a gas (or is made into sulfuric acid), and the iron into ferrous silicate, which is removed as slag.

454. Metallurgy of copper-iron-sulfide ores. — Let us consider six steps in detail by using Fig. 203.

1. *Crushing.* The ore is first crushed to the proper size in *A*.

2. *Concentrating.* The crushed ore is next concentrated by grinding, washing, shaking, settling, and floating. By these operations useless parts of the ore are removed and three general sizes result: (a) The coarse concentrate, which goes from the shaking machine *B* to the blast furnace *M*. (See 4 (2).) (b) The fine concentrate, which, after the grinding in *C* and shaking in *D*, goes to the roasting furnace *K*. (c) The very fine concentrate, which is further concentrated. The ground ore from *E* passes through the desliming cone *F* on to the

table *G*; here part goes to the roasting furnace *K*. The rest is ground exceedingly fine in the mill *H* and goes on into the flotation machine *I-J* (Fig. 204). Here a remarkable change occurs. The fine ore particles

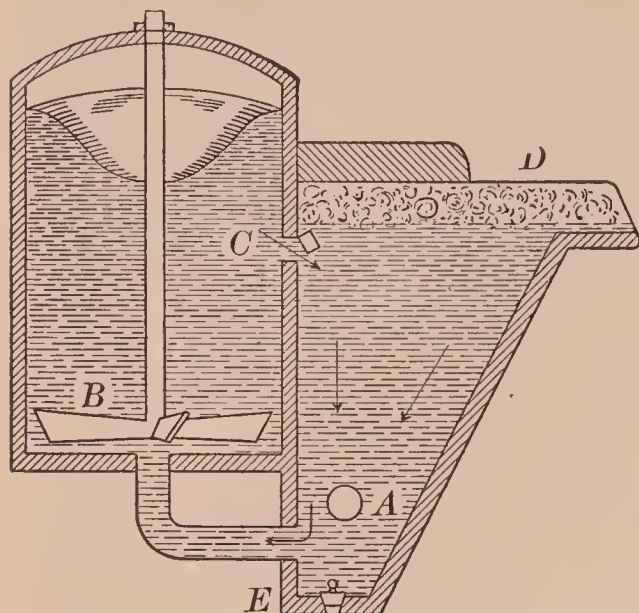


FIG. 204. — Section of a flotation apparatus.

are mixed with water containing a little oil (and sometimes sulfuric acid). Air is beaten into the mixture by vigorous agitation. An oily froth is formed to which the particles of copper ore stick and float on the top of the mass, whereas the rocky particles sink. The water is removed (by a filter — not shown) and the concentrate goes to the roasting furnace *K*.

3. *Roasting.* The charge is heated red-hot but not melted; the heat, after the furnace is once started, comes from the burning sulfur. By this treatment most of the sulfur is

removed and part of the copper and iron sulfides are changed into oxides. The product goes to the reverberatory furnace *L*.

4. *Smelting.* The product from the roasting furnace *K* is smelted in the reverberatory furnace *L*; and the coarse concentrate from the jig *B* is smelted in the blast furnace *M*. That is, they are heated with a flux until they melt, just as iron is smelted. By this treatment more sulfur (as sulfur dioxide) and iron (as slag) are removed, and the copper and iron sulfides melt together to form copper **matte**. There are two kinds of furnaces for smelting:

(1) In the **reverberatory furnace** *L* the heat radiated down upon the hearth fuses the charge (Fig. 205). Most of the iron sulfide becomes iron oxide and forms a slag with the lime, silica, and alumina (Al_2O_3) in the charge, while the copper sulfide and the remaining iron sulfide melt together and sink through the slag to the bottom of the mass. The slag runs off continually. The matte is tapped off periodically and taken to the converter *N*.

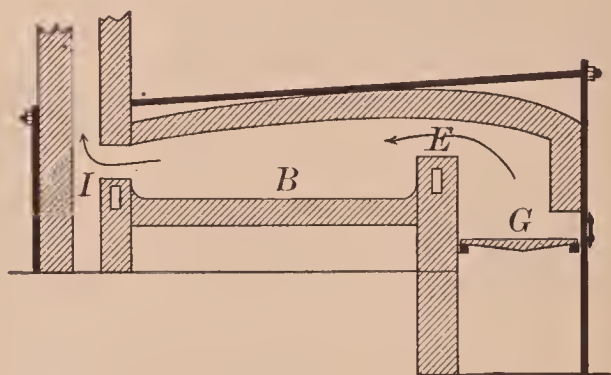


FIG. 205. — Reverberatory furnace. The fire burns on the grate *G*, and the long flame which passes over the bridge, *E*, is reflected down by the sloping roof upon the contents of the furnace. Gases escape through *I*. The charge, which rests upon *B*, does not come in contact with the fuel.

(2) The blast furnace *M* is much like that used in making cast iron (Figs. 126, 127, 128), though it is cooled by a constant flow of water through jackets which inclose its sides. The charge consists of the coarse concentrate (see 2 (*a*) above), limestone, and coke. Air is blasted through the furnace. Much heat is supplied by the burning sulfur. By this treatment much of the sulfur is removed and most of the iron forms a slag with the limestone in the charge or with the silica and alumina purposely left in the concentrate. The copper sulfide melts with the rest of the iron sulfide into copper matte, which goes to the converter *N*.

5. *Converting.* This is the last stage. Matte from the reverberatory and blast furnaces (*L* and *M*) is poured into the converter — 65 tons to

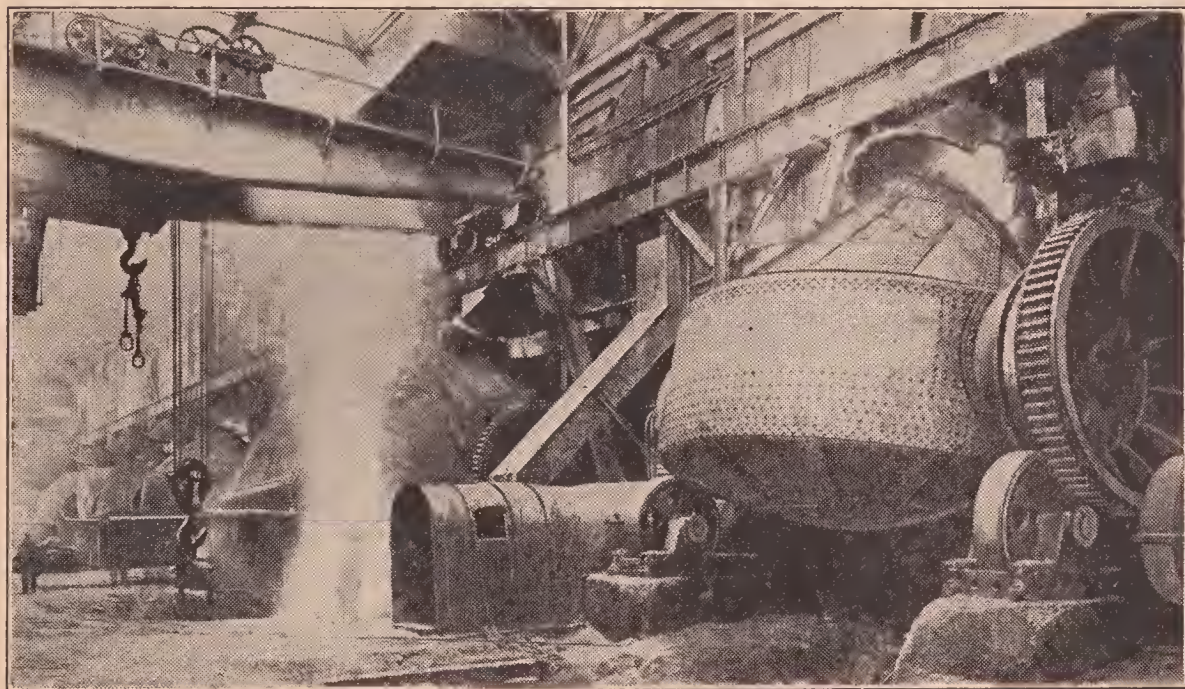


FIG. 206. — A copper converter in action.

a charge (Fig. 206). The converter is lined with magnesia brick. Air is blown through the liquid mass. The remaining sulfur burns to sulfur dioxide which escapes through the top, while the iron forms a slag with the silica and alumina in the ore (or added to supply these substances). The product, which is metallic copper together with a little iron, sulfur, and slag, goes to the refining-casting furnace *O*.

6. *Casting into anodes.* The product from the converter *N* is further purified in the refining-casting furnace *O* by blowing air through it and then stirring it with poles of green wood to reduce any oxide. When the refining is complete, the copper, now 99.25 per cent pure and called **blister copper**, is cast into anodes. The anodes weigh about 500 pounds each. They are sent to the refinery for final purification by electrolysis.

455. Refining of copper by electrolysis. — Since very pure copper (at least 99.95 per cent) is needed in electrical indus-

tries, the blister copper must be further purified to remove the last traces of silver, gold, and other impurities. This is done by electrolysis, and the refined metal, which is 99.98 per cent pure, is called **electrolytic copper**.

The anodes are suspended in a solution of copper sulfate and sulfuric acid. The cathodes, which are made of thin sheets of pure copper (coated with graphite), also dip into the solution between the anodes (Fig. 207). When the current passes, copper ions (Cu^{++}) migrate to the cathode, lose their charges, and are deposited as metallic copper, thus building up the cathode (Fig. 208). An equal weight of copper dis-

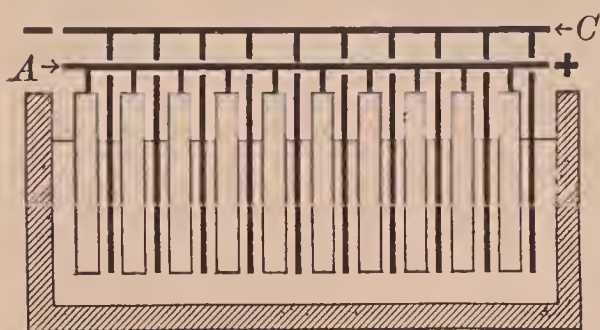


FIG. 207. — Sketch of the apparatus for the preparation of pure copper by electrolysis. A, A, A are anodes, and C, C, C are cathodes.

solves from the anode, which gradually wears away. Only copper is deposited on the cathode. The gold and silver and other substances drop to the bottom of the cell as a slime; from this slime the gold, silver, and other substances which were left in the copper anodes are profitably extracted.

456. Properties of copper. — Copper is distinguishable from all other metals by its peculiar reddish color. It is flexible, ductile, malleable, and tough, and hence can be shaped into many forms. It melts at 1083°C . Its specific gravity is 8.9. Copper is an excellent conductor of electricity — the best of the cheaper metals.

Exposed to ordinary air, it turns dull owing to a thin film of oxide. In moist air it gradually becomes coated with a green (basic) copper carbonate. Heated in the air, it is first changed into black copper oxide (CuO), and at a high temperature it burns, and colors a flame emerald-green.

Copper, unlike other common metals, *e.g.*, magnesium, zinc, and iron, does not liberate hydrogen from acids (§§ 68, 72). With nitric acid it forms copper nitrate and nitrogen oxides (§ 203); with hot sulfuric acid it yields copper sulfate and sulfur dioxide (§ 217). Hydrochloric acid has little effect upon it. Sea water attacks it, forming a (basic)

cupric chloride; hence the copper sheathing of vessels corrodes.

Copper displaces certain metals from their solutions (§ 462). A clean copper wire, if placed in a solution of any mercury compound, soon becomes coated with mercury. On the other hand, metals like iron, zinc, and magnesium displace copper from its solution, *e.g.*, a nail or a knife blade soon becomes coated with copper if dipped into a solution of any copper compound. Scrap iron is used to precipitate copper on a large scale in some copper refineries.

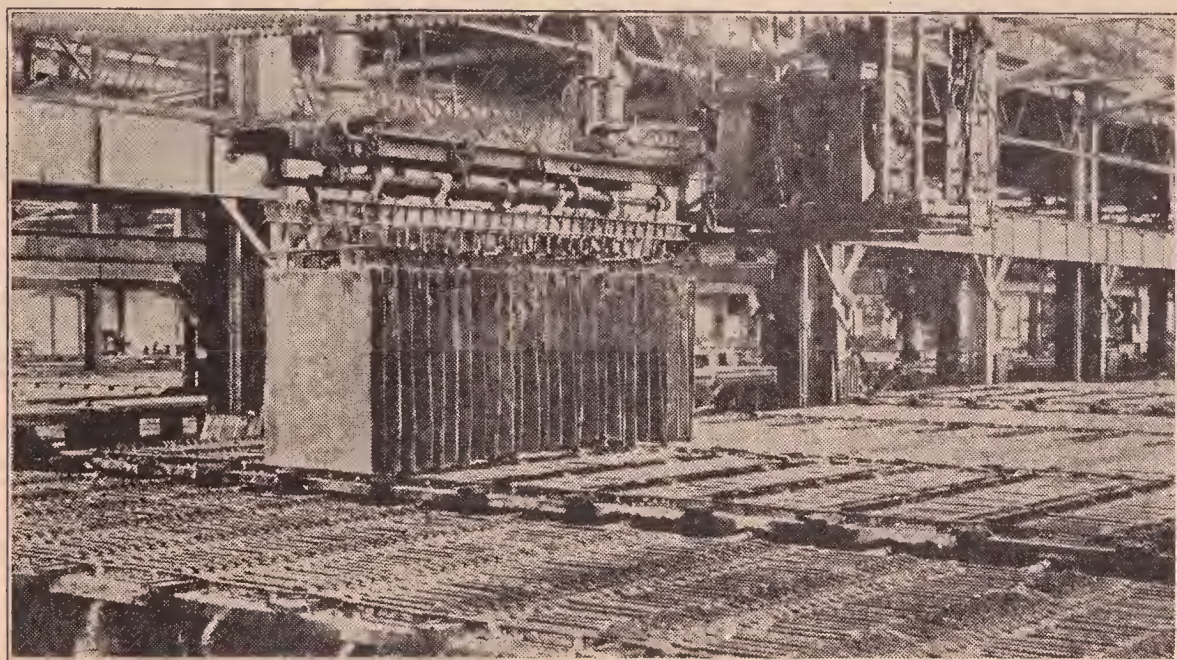


FIG. 208. — Removing cathodes of pure copper from a cell in one of the rooms of an electrolytic refining plant.

457. Tests for copper. — (1) The reddish color, peculiar “coppery” taste, and green color imparted to a flame serve to identify metallic copper. (2) An excess of ammonium hydroxide added to a solution of a copper compound produces a beautiful deep blue solution. (3) A few drops of acetic acid and potassium ferrocyanide ($\text{K}_4\text{Fe}(\text{CN})_6$) added to a dilute solution of a copper compound precipitate brown copper ferrocyanide ($\text{Cu}_2\text{Fe}(\text{CN})_6$).

458. Uses of copper. — Large quantities of copper wire are used to conduct electricity, *e.g.*, in operating the telegraph, cable, telephone, radio, electric railway, and electric light. Sheet copper is made into household utensils, boilers,

and stills, and is also used for roofs and spouts. Most nations use copper as the chief ingredient of small coins. Much copper is utilized in electrical and other apparatus, especially now that copper can be cast without blowholes. Books are printed and illustrated from electrotpe plates made by depositing copper upon an impression of the type or design in wax.

Copper alloys. — Copper is an ingredient of many common and useful alloys, *e.g.*, bronze, brass, and monel metal (Fig. 209). (See Table XXI.)

TABLE XXI. — COPPER ALLOYS

NAME	COPPER	ZINC	ALU- MINUM	SILVER AND GOLD	NICKEL	TIN
Aluminum bronze	90-98	—	2-10	—	—	—
Bell metal	78	—	—	—	—	22
Brass	63-93	5-40	—	—	—	—
Bronze	60-95	25	—	—	—	3-8
German silver	50-60	—	—	—	6-20	—
Gun metal	90	—	—	—	—	10
Gold coin	10	—	—	Gold 90	—	—
Monel metal	28	—	—	—	69	—
Nickel coin	75	—	—	—	25	—
Silver coin	10	—	—	Silver 90	—	—

459. Cuprous and cupric compounds. — Copper forms two series of compounds — the cuprous and the cupric. The valence of copper is + 1 in cuprous compounds and + 2 in cupric.

Cupric salts are more common. All dilute solutions of ordinary cupric salts are blue owing to the presence of the blue cupric ion (Cu^{++}).

Soluble copper compounds are more or less poisonous. Cooking utensils made of copper should be used with care. Vegetables, acid fruits, and preserves, if boiled in them, should be removed as soon as cooked. The vessels themselves should be kept bright to prevent the formation of copper salts, which might contaminate the contents. Certain lower forms

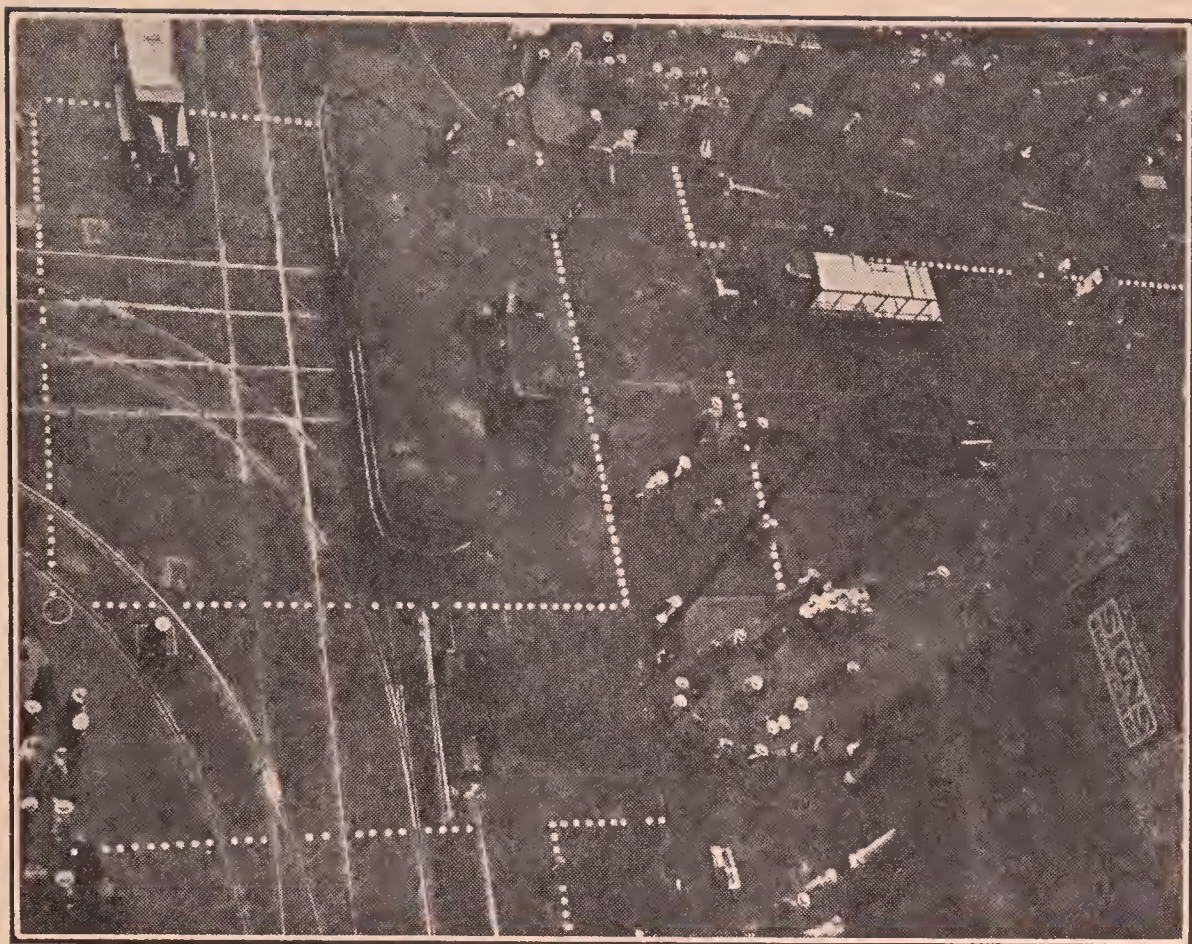


FIG. 209. — Monel metal traffic markers (white spots) on a crowded “loop” in Chicago.

of plant life (algæ) are poisoned by copper salts. Copper sulfate is sometimes added to ponds and reservoirs to destroy such growths, and thereby render the water suitable for drinking.

460. Copper sulfate or cupric sulfate. — This is a blue solid. It is also called blue vitriol or bluestone. Copper sulfate solutions have an acid reaction owing to hydrolysis (§ 281). (See also § 86.)

Copper sulfate is used in electric batteries (*e.g.*, the gravity cell), in making other copper salts, and in copper plating and electrotyping. A mixture of copper sulfate and milk of lime, called **Bordeaux mixture**, is sprayed upon trees to destroy fungi and kill insects.

Copper sulfate is prepared by treating copper scrap in the air with warm, dilute sulfuric acid or by oxidizing copper sulfide. Some of the copper sulfate of commerce is a by-product in refining gold and silver with sulfuric acid.

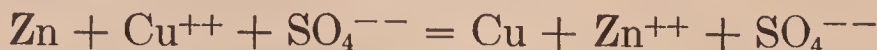
461. Other copper compounds. — **Cuprous oxide** (Cu_2O) is precipitated as a reddish powder by heating Fehling's solution (*i.e.*, a mixture of solutions of copper sulfate, sodium citrate, and sodium carbonate) with glucose; its formation serves as a **test for glucose** and sugars like it (§ 258). **Cupric oxide** (CuO) is a black solid formed by heating copper in air. It is used to remove sulfur compounds from petroleum. **Copper nitrate** ($\text{Cu}(\text{NO}_3)_2$) is a blue, crystallized solid, formed by the interaction of copper and dilute nitric acid. It is a cupric salt. **Copper bromide** (CuBr_2) is a black crystallized solid, which in dilute solutions is blue (due to Cu^{++}) and in concentrated solution is brown (due to CuBr_2).

462. Displacement of metals. — We have already seen that iron, zinc, and other metals displace copper from copper salt solutions, and that copper itself displaces mercury (§ 456). The deposition of metallic copper and of mercury are examples of a chemical change in which most metals can participate. It has been found that the metals can be arranged in the order in which one metal can displace another from its solution. This order is sometimes called the **displacement series**. The arrangement of the common metals is shown in the accompanying list (compare § 72). In this series each free metal displaces succeeding metals from their solutions. (Read horizontally.)

DISPLACEMENT SERIES OF THE COMMON METALS

Magnesium	Aluminum	Zinc	Iron	Tin	Lead
Hydrogen	Copper	Mercury	Silver	Platinum	Gold

An ionic equation for an example of displacement is: —



Hydrogen is not a metal in the common acceptance of this term. But it is usually included in the displacement series of metals, because the metals that precede hydrogen displace it from most acids (§ 68). That is, hydrogen behaves in this respect like the members of the series. Recall that hydrogen is like metals in that it forms positive ions (H^+).

EXERCISES

1. Prepare a summary of the metallurgy of copper-iron sulfide ores.
2. Interpret the electrolytic refining of copper.
3. State physical properties of copper that fit it for electrical uses.
4. Give three tests for copper.
5. Write the formulas of the following compounds by applying the principle of valence: Cupric bromide, cuprous chloride, cupric phosphate, cupric sulfate, cuprous iodide.

PROBLEMS

1. Calculate the weight of copper in 10 gm. of crystallized copper sulfate.
2. Calculate the simplest formulas corresponding to: (a) Cu = 96.94, H = 3.05; (b) Cu = 57.46, H = 0.91, O = 36.2, C = 5.43.
3. How much copper can be obtained from an American ten cent coin which weighs 2.44 gm.?
4. A certain weight of copper oxide, when heated in a current of hydrogen, lost 59.789 gm. of oxygen and formed 237.55 gm. of copper. If the atomic weight of oxygen is 16, calculate the atomic weight of copper.

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

- | | |
|----------------|---|
| Exercise S4 | — Preparation of Copper Oxide. |
| Exercise *6 | — Reduction of Copper Oxide by Carbon. |
| Exercise *10 | — Reduction of Copper Oxide by Illuminating Gas. |
| Exercise S10 | — Reduction of Copper Oxide by Hydrogen — T. |
| Exercise 12 | — Test for Copper ((1) part only). |
| Exercise *14 I | — Solubility of Solids. |
| Exercise *18 A | — Water of Hydration (Copper Sulfate). |
| Exercise S13 | — Anhydrous Compounds (Copper Sulfate). |
| Exercise S15 | — Efflorescence and Deliquescence (Copper Sulfate part only). |
| Exercise 22 | — Formation of Copper Sulfide. |
| Exercise 33 | — Electrolysis of Copper Sulfate Solution — T. |
| Exercise S31 | — Electrolysis of Copper Sulfate Solution (Short Method) — T. |
| Exercise 35a | — Colored and Colorless Ions. |
| Exercise 34 | — Hydrolysis of Certain Salts (Copper Sulfate only). |
| Exercise *39 | — Nitric Acid and Copper (III only). |
| Exercise S38 | — Sulfides (Copper part of (a)). |
| Exercise 54 | — Cuprous Oxide. |
| Exercise 62c | — Flame Tests for Metals. |
| Exercise S56 B | — Tests for Metals (Copper). |

TOPIC XXIII: MAGNESIUM—ZINC—MERCURY

463. Physical and chemical properties of magnesium. — Magnesium is a lustrous, silvery white metal. It is light, the specific gravity being 1.75. It is tenacious and ductile, and when hot can be drawn into wire or rolled into a ribbon, the latter being a common commercial form.

Heated in air, it burns with a dazzling light and produces magnesium oxide (MgO) together with a little magnesium nitride (Mg_3N_2). It does not tarnish in dry air, but in

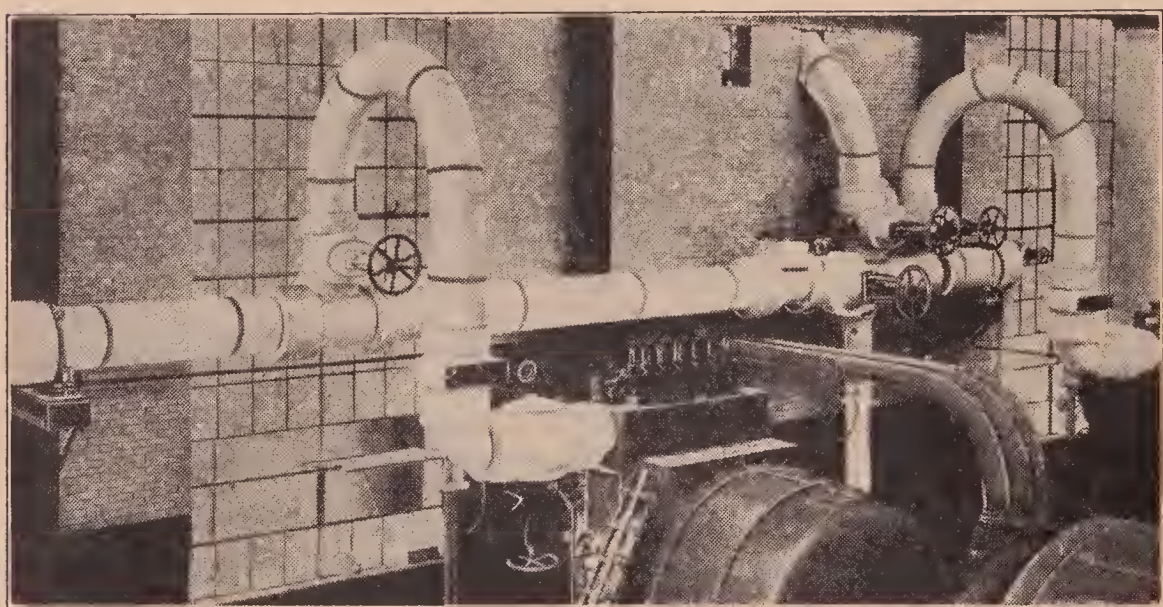


FIG. 210. — Pipes covered with "85 per cent magnesia" to prevent loss of heat.

moist air it is soon covered with a film of the (basic) carbonate. It liberates hydrogen from acids (§ 72). It also liberates hydrogen, slowly, from boiling water (§ 69). Solutions of magnesium salts contain magnesium ions (Mg^{++}).

464. Uses of magnesium. — The light from burning magnesium affects a photographic plate, and magnesium powder (mixed with potassium chlorate) is used in taking flashlight photographs. The powder is one ingredient of the mixture used in signal lights (*e.g.*, star shells) and fireworks. Magnesium and its alloys are used to construct articles needing a light durable framework. **Magnalium** is an alloy of magnesium and aluminum (§ 504).

465. Magnesium oxide and hydroxide. — Magnesium oxide (MgO) is a white, bulky powder. It is formed when magnesium burns in the air, *e.g.*, in taking a photograph with a flashlight powder. It is manufactured by gently heating magnesium carbonate, somewhat as lime is made from limestone (§ 293). It is called **magnesia**, or calcined magnesia, though commercial magnesia is a complex compound (largely $\text{Mg}(\text{OH})_2 \cdot 3 \text{MgCO}_3$). Like lime, magnesia is infusible and is used in making fire brick, crucibles, and furnace linings. It is a poor conductor of heat, and is the main ingredient of a mixture called “85 per cent magnesia,” which is used to insulate pipes and boilers and thereby prevent the loss of heat (Figs. 210, 211).

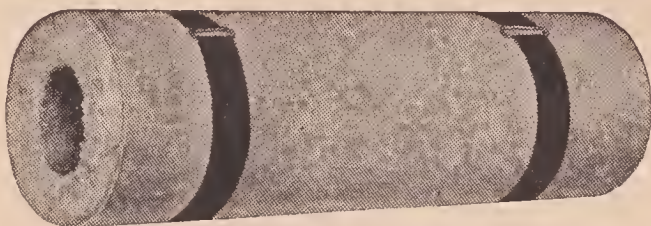


FIG. 211. — Section of a pipe showing end of protective cover.

Magnesium oxide unites slowly with water and forms magnesium hydroxide ($\text{Mg}(\text{OH})_2$), which is a white solid. It is only very slightly soluble in water, and a suspension, called **milk of magnesia**, is used as a medicine to neutralize acidity in the stomach. Magnesium hydroxide is also an ingredient of some kinds of tooth paste.

466. Magnesium sulfate and chloride. — Magnesium sulfate (MgSO_4) is a white solid. The commercial form is often called **Epsom salts** ($\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$). It is very soluble in water and its solution has a bitter taste; it is used as a purgative. Magnesium sulfate, like calcium sulfate, causes permanent hardness in water (§ 298). **Magnesium chloride** (MgCl_2) is a white solid. The crystallized salt ($\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$) is very deliquescent. It is one of the ingredients which make common salt moist. Magnesium chloride causes permanent hardness in water. If water containing magnesium chloride, *e.g.*, sea water, is used in a boiler, magnesium hydroxide and hydrochloric acid are formed. The insoluble magnesium hydroxide becomes a hard scale and the hydrochloric acid corrodes the metal. Hence water containing magnesium chloride (or sulfate) is highly objectionable and should be softened before use.

ZINC

467. Occurrence of zinc. — The chief ores are zinc sulfide (sphalerite, zinc blende, ZnS) and zinc carbonate (smithsonite, ZnCO_3).

468. Metallurgy of zinc. — The ores are usually concentrated (sulfide ore by the flotation process (§ 453, 2 (c))), then roasted to form the oxide, which is reduced by heating with finely powdered coal.

The reduction is conducted in special shaped earthenware retorts (*A*) connected with double receivers (Fig. 212). At first the zinc condenses in *C* as a powder called zinc dust. But when this receiver becomes hot, the zinc condenses to a liquid in *B*, from which it is drawn off at intervals and cast into bars or plates. The impure zinc, called

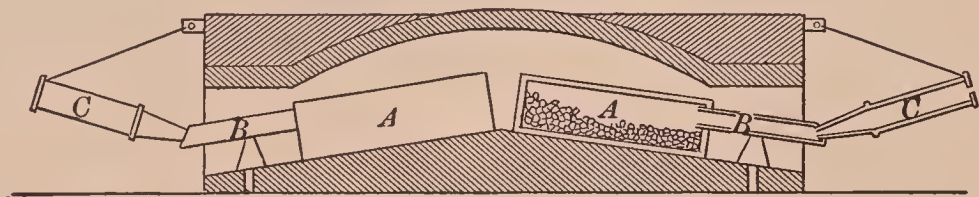


FIG. 212. — Retorts for reduction of zinc oxide (open — right, closed — left).

spelter, is freed from carbon, lead, iron, cadmium, and arsenic by repeated distillation; very pure zinc is obtained by the electrolysis of a zinc salt (Fig. 213).

469. Physical and chemical properties of zinc. — Zinc is a bluish white, lustrous metal. At ordinary temperatures it is rather brittle, but at $100\text{--}150^\circ\text{C}$. it is soft and can be rolled into sheets and drawn into wire; zinc which has been rolled or drawn does not become brittle on cooling. It melts at 419°C . If melted zinc is poured into water, it forms irregular brittle lumps called **granulated zinc**, which is a convenient form for use in the laboratory.

Heated in air above its melting point, zinc burns with a bluish green flame, forming white zinc oxide (ZnO). Zinc does not tarnish in dry air, but ordinarily it becomes coated with a thin, non-porous film of basic zinc carbonate. Zinc interacts readily with acids and usually liberates hydrogen (§ 68, but see §§ 200, 203). With hot solutions of sodium

and potassium hydroxides, it forms zincates and hydrogen, thus : —



Zinc displaces most metals from their solutions (§ 462). Ordinary zinc salts yield zinc ions (Zn^{++}) in solutions.

470. Uses of zinc. — Zinc is extensively used as an electrode in many kinds of batteries. Sheet zinc is used for roofs, gutters, pipes, parts of washing machines, and as a lining for tanks.

The chief use of zinc is in making **galvanized iron**. This is iron covered with a thin layer of zinc and is made by dipping clean sheet iron into melted zinc. The zinc protects the iron from air and moisture. Galvanized iron, if properly manufactured, does not rust easily and is extensively used for netting, wire, roofs, pipes, cornices, and water tanks.

Zinc shavings are used in the cyanide process of extracting gold (§§ 494,

495). Zinc is an ingredient of many useful alloys, *e.g.*, brass, bronze, and German silver (§ 458).

471. Zinc oxide. — The pure oxide (ZnO) is white when cold and yellow when hot. It is formed when zinc burns, and is manufactured in this way or by heating zinc carbonate. It is often called zinc white or Chinese white, and large quantities are used as a filler in the manufacture of automobile tires and white rubber goods.

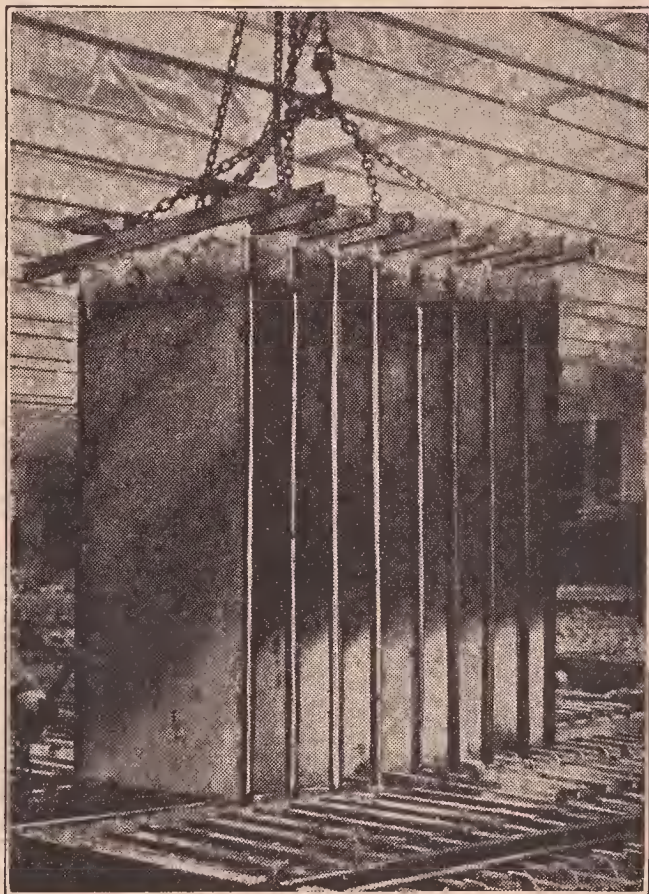


FIG. 213. — Lifting the cathodes of pure zinc from an electrolytic cell.

Zinc oxide is also used to make white paint. Paint made of zinc oxide, unlike paint made of lead compounds, is not darkened by sulfur compounds in the atmosphere (§ 520).

On account of its antiseptic and drying properties, zinc oxide is an ingredient of ointments.

472. Zinc hydroxide. — This is formed as a dull white precipitate by the interaction of a small amount of sodium or potassium hydroxide and a solution of a zinc salt. An excess of the alkaline hydroxide changes zinc hydroxide into a zincate (§ 469, end). Zinc hydroxide has both acid and basic properties. It dissolves in ammonium hydroxide owing to the formation of a soluble complex compound called zinc ammonia (or ammonio-) hydroxide ($\text{Zn}(\text{NH}_3)_4(\text{OH})_2$).

473. Zinc sulfide, sulfate, and chloride. — Pure zinc sulfide (ZnS) is white, and is formed as a jelly-like precipitate when hydrogen sulfide is passed into a solution of a zinc salt. A mixture of zinc sulfide and barium sulfate, called **lithopone**, is used as a white pigment in paints for interior work.

The **sulfate** (ZnSO_4) is formed by the interaction of zinc and dilute sulfuric acid. Large quantities are also made by roasting the sulfide in a limited supply of oxygen and extracting the sulfate with water. Thus prepared, it is a white, crystallized solid ($\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$) called **white vitriol**. It is used in dyeing, as a disinfectant, and as a medicine. Like other zinc salts, it is poisonous.

The **chloride** (ZnCl_2) is a white, deliquescent solid. Large quantities are used to preserve wood, especially posts and railroad ties.

474. Tests for zinc. — The precipitation of the sulfide or hydroxide, as above described, serves as a **test for zinc**. A green incrustation is produced when zinc compounds are heated on charcoal and then moistened with cobaltous nitrate solution. (Compare § 506, last paragraph.)

MERCURY

475. Metallurgy of mercury. — Mercury is prepared by roasting cinnabar (HgS) in a current of air, and condensing the vapor of the metal.

476. Physical and chemical properties of mercury. — Mercury is a silvery metal, and is the only common one that is liquid at ordinary temperatures. Its common name “quicksilver” emphasizes these properties. It solidifies at -38.7°C . and boils at 357°C . It is a heavy metal, the specific gravity being about 13.6. Mercury is a good conductor of electricity.

Mercury does not tarnish in the air, unless sulfur compounds are present. At about 300°C . it combines slowly with oxygen to form red mercuric oxide (HgO). Hydrochloric acid and cold sulfuric acid do not affect it; hot concentrated sulfuric acid changes it into mercuric sulfate (HgSO_4). Nitric acid changes it into nitrates — hot acid into mercuric nitrate ($\text{Hg}(\text{NO}_3)_2$) and cold dilute acid, with an excess of mercury, into mercurous nitrate (HgNO_3). It is displaced from solution by many metals (§ 462), and also displaces some, *e.g.*, a copper wire becomes coated with mercury when put into a solution of a mercury compound.

477. Amalgams. — Alloys of which mercury is a component are called **amalgams**. Amalgamated zinc is used in certain electric batteries to prevent unnecessary loss of the zinc. Amalgams of some metals (*e.g.*, tin, silver, gold) are used as a filling for teeth. Silver and gold form amalgams readily, and considerable mercury is used in extracting these precious metals from their ores (§§ 483, 494). Care should be taken, while using mercury, not to let it come in contact with jewelry.

478. Uses of mercury. — Mercury is used in thermometers, barometers, mercury-vapor lamps and illuminated signs, and high vacuum air pumps. Considerable is used in preparing certain explosives, *e.g.*, mercury fulminate, which is used in percussion caps and detonators to explode powder and nitroglycerin.

The use of mercury in thermometers depends on several facts, *e.g.*, it is heavy, bright liquid and has a uniform change of volume with a change of temperature (between a wide range of temperature). The curve showing the relation of volume and temperature is almost a straight line (Fig. 214), that is, the expansion of mercury is regular.

479. Two series of mercury compounds. — Mercury, like copper and iron, forms two classes of compounds — **mercurous** and **mercuric**.

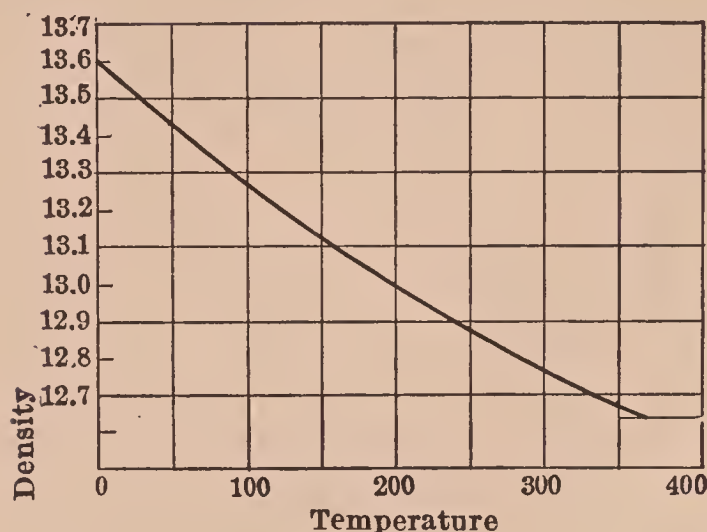


FIG. 214. — Curve showing regular change in volume of mercury with change of temperature.

The valence of mercury is + 1 in mercurous compounds and + 2 in mercuric. Solutions of mercurous salts contain mercurous ions (Hg^+), and of mercuric salts, mercuric ion (Hg^{++}).

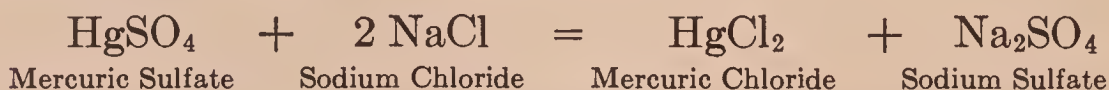
480. Mercurous and mercuric chlorides. — The mercurous salt (HgCl) is a white, tasteless

powder, insoluble in water. It is used as a medicine under the name of **calomel**. It is formed as a white precipitate when a chloride and mercurous nitrate interact — a **test for mercury in mercurous ions** (Hg^+). The equation is : —



This test is confirmed by adding ammonium hydroxide which blackens the precipitate.

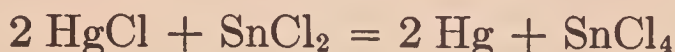
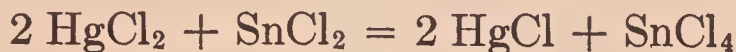
The **mercuric** salt (HgCl_2) is a white, soluble, crystalline solid. It is manufactured by heating a mixture of mercuric sulfate and sodium chloride, thus : —



Mercuric chloride is a violent poison. The best antidote is the white of a raw egg. The albumin forms an insoluble mass with the poison.

The common name of mercuric chloride is **corrosive sublimate** (or bichloride of mercury). It has powerful antiseptic properties, and a dilute solution (1 gm. in 1000 gm. of water) is extensively used in surgery to sterilize instruments and to protect wounds from infection.

Mercuric chloride, when treated carefully with stannous chloride, is reduced first to white mercurous chloride and finally to a dark gray precipitate of finely divided mercury — the test for mercuric ions (Hg^{++}). The equations for these reactions are: —



EXERCISES

1. State the properties and uses of magnesium.
2. Write equations for (a) interaction of magnesium and sulfuric acid and (b) heating magnesium in nitrogen.
3. Describe the metallurgy of zinc.
4. Summarize the (a) physical and (b) chemical properties of zinc.
5. What are the tests for zinc?
6. What are the tests for (a) mercury, (b) mercurous compounds, (c) mercuric compounds.
7. Describe (a) mercurous chloride and (b) mercuric chloride. What is the commercial name of each? The use?
8. What is (a) magnesia, (b) Epsom salts, (c) galvanized iron, (d) Chinese white, (e) white vitriol, (f) calomel, (g) corrosive sublimate?
9. Write the ordinary and the ionic equations for (a) mercuric chloride and hydrogen sulfide form mercuric sulfide and hydrochloric acid, (b) magnesium chloride and sodium hydroxide form magnesium hydroxide and sodium chloride, (c) zinc hydroxide and sodium hydroxide form sodium zincate and water, (d) mercuric chloride and stannous chloride form mercurous chloride and stannic chloride.
10. Write the formulas of the following compounds by applying the principle of positive and negative valence, or by utilizing analogous formulas in this chapter: Magnesium bromide, magnesium nitrate, magnesium sulfide, zinc chromate, zinc carbonate, zinc acetate, zinc phosphate (ortho), mercurous fluoride, mercuric sulfate, mercurous oxide.

PROBLEMS

1. Calculate the per cent of the metallic element in (a) magnesium oxide, (b) zinc oxide, and (c) mercuric oxide.
2. Calculate the atomic weights of magnesium, mercury, and zinc: (a) 16.0263 gm. of MgO give 47.8015 gm. of MgSO_4 ; (b) 16.03161 gm. of zinc give 19.9568 gm. of ZnO ; (c) 118.3938 gm. of HgO give 109.6308 gm. of mercury. (Use exact atomic weights.)

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

- Exercise 1b — Properties and Chemical Change.
Exercise *21 — Equivalent Weight of Magnesium.
Exercise S56 C — Test for Magnesium.
Exercise S58c — Cobalt Nitrate Tests (Magnesium).
Exercise S9c — Test for Zinc — T.
Exercise 20 — Equivalent Weight of Zinc.
Exercise S33c — Testing for Ions (Zinc).
Exercise S34 — Hydrolysis of Certain Salts (Zinc).
Exercise *61c — Displacement of Metals (Zinc).
Exercise 62d — Flame Tests for Metals (Zinc).
Exercise S56 D — Tests for Metals (Zinc).
Exercise S58b — Cobalt Nitrate Tests (Zinc).
Exercise S1 — Decomposition of Mercuric Oxide.
Exercise *61a — Displacement of Metals (Mercury).
Exercise S56 E — Tests for Metals (Mercury).
Exercise S62 — Qualitative Analysis.

TOPIC XXIV: SILVER — PHOTOGRAPHY — GOLD

481. Introduction. — Silver and gold are precious metals. They have been used for ages in the form of ornaments, costly vessels, and coins. The Latin names of these metals are *argentum* and *aurum*, from which the symbols Ag and Au are derived.

SILVER

482. Occurrence of silver. — The chief ore is silver sulfide (argentite, Ag_2S), which is usually associated with lead sulfide and other complex sulfide ores. In fact, silver-bearing ores are the main source of silver.

483. Metallurgy of silver. — 1. Ores containing free silver, or silver compounds that can be easily changed into silver, are treated by the **amalgamation process**. The powdered ore is first changed, if necessary, into silver chloride by roasting with sodium chloride. The silver is displaced from the chloride by agitation with water and iron (or an iron compound), and then is extracted by adding mercury, which forms an amalgam with the silver (§ 477). When the amalgam is heated, the mercury distills off and the silver remains behind.

2. In the **Parkes process** sulfur, arsenic, and other impurities are removed by roasting. The final mixture of lead, silver, and gold is

melted with about 1 per cent of zinc. As the mixture cools, an alloy of silver, gold, zinc, and a little lead rises to the surface, solidifies, and is skimmed off. The skimmings are heated in a retort to volatilize the zinc, and then in a shallow furnace (cupel furnace) to convert the lead into an oxide (PbO), which melts and runs off, leaving an alloy of silver and gold (§ 495 and Fig. 220). This latter process of removing lead is called **cupellation**. Silver and gold are separated by electrolysis (§ 495).

3. In the **cyanide process** pulverized ore is mixed with dilute sodium cyanide solution. The silver forms silver cyanide (AgCN) which reacts with the excess of sodium cyanide to form soluble sodium silver cyanide ($\text{NaAg}(\text{CN})_2$). Zinc is added to precipitate the silver (§ 462), thus: —



4. Silver can be separated from its alloy with gold by several processes. (a) In the **older process** the alloy is boiled with concentrated nitric (or sulfuric) acid; the silver forms a soluble silver salt (nitrate or sulfate) but the gold is not acted upon. The silver is precipitated from the diluted solution by metallic copper. (b) In the electrolytic process the anode is a silver-gold alloy rich in silver and the solution is silver nitrate in nitric acid; the silver ion migrates to the cathode, and is deposited, while the gold is left as a powder or skeleton at the anode (§ 495).

484. Properties of silver. — Silver is a lustrous, white metal. It is harder than gold, but softer than copper. It is ductile and malleable, and can be easily made into various shapes. Silver has a specific gravity of about 10.5, being heavier than copper, but lighter than lead. It melts at 960°C . Silver conducts electricity the best of all metals, but it is too expensive for general use.

485. Chemical properties of silver. — Silver does not tarnish in air unless hydrogen sulfide is present, and then the familiar brown (or black) film of silver sulfide (Ag_2S) is produced. It also turns black when in contact with organic sulfur compounds, *e.g.*, those in perspiration, vulcanized rubber, eggs, and mustard. The tarnishing of household silver is caused by hydrogen sulfide in illuminating gas or gas from burning coal.

Certain metals, *i.e.*, those higher in the displacement series (§ 462), precipitate silver from its solutions.

Silver is only very slightly acted upon by hydrochloric acid, and not at all by molten sodium hydroxide, potassium hy-

dioxide, or potassium nitrate. Nitric acid and hot concentrated sulfuric acid change it into the nitrate (AgNO_3) and sulfate (Ag_2SO_4) respectively. Sodium cyanide in the presence of air and water changes it into sodium silver cyanide ($\text{NaAg}(\text{CN})_2$).

Solutions of simple silver salts contain silver ions (Ag^+), whereas complex salts yield complex ions, *e.g.*, the silver-cyanogen ion ($\text{Ag}(\text{CN})_2^-$) and the silver-ammonia ion ($\text{Ag}(\text{NH}_3)_2^+$).

486. Cleaning silverware. — Tarnished silverware can be cleaned by rubbing off the film of sulfide with a very soft abrasive — “silver polish.” It can be safely and quickly cleaned by an electrolytic process, which has largely replaced the old process. A piece of metallic aluminum and the tarnished object are immersed in a hot solution of sodium bicarbonate and sodium chloride, and kept *in contact*. The cleaning is soon accomplished. The object is removed, thoroughly washed in clean, hot

water, and dried. The proportions for household use are a teaspoonful each of baking soda and common salt to a quart of water. The best results are obtained when the solution is very hot and the two metals are in good contact.



Courtesy Eastman Kodak Co.

FIG. 215. — Bars of silver in a large photographic plant ready for making into silver nitrate.

and are called “900 fine.” British silver coins were formerly “925 fine.” This quality is called **sterling silver**, and from it much ornamental and useful silverware is made. Large quantities of silver are used to plate other metals and to make silver compounds, especially silver nitrate (Figs. 215, 217).

487. Uses of silver. — Silver is too soft for constant use, and is hardened by adding a small amount of copper. These alloys are used as coins and for jewelry. Silver coins of the United States contain 900 parts of silver to 100 parts of copper,

488. Silver plating. — The object to be plated is cleaned, and made the cathode in a solution of potassium (or sodium) silver cyanide; the anode is a plate of pure silver (Fig. 216). When the electric current is passed, the silver dissolves from the anode and deposits on the cathode. The deposit of silver is dull, and is brightened by rubbing.

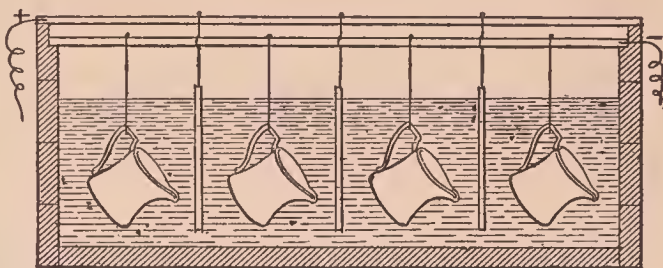
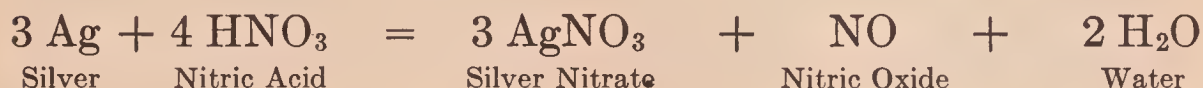


FIG. 216. — Silver plating.

Mirrors and reflectors (especially for automobiles) are made by coating glass with silver. A mixture of silver nitrate and ammonium hydroxide is reduced to metallic silver, which sticks to the glass and is protected by varnish.

489. Silver nitrate. — This is a white crystalline solid, made from silver and nitric acid (Fig. 217). The equation is:—



Courtesy Eastman Kodak Co.

FIG. 217. — Making silver nitrate.

It is soluble in water. It turns dark in contact with organic matter owing to partial reduction to metallic silver. For this reason it blackens the skin; if applied long enough, it disintegrates the flesh, and is used by surgeons to cauterize sores or abnormal growths.

490. Silver halides. — The chloride, bromide, and iodide are formed as curdy precipitates when the silver ion (Ag^+) unites with the halide ion (Cl^- , Br^- , I^-). The **chloride** (AgCl) is a white, curdy solid, which soon turns violet and finally brown in the light. It is converted by ammonium hydroxide into a soluble compound ($\text{Ag}(\text{NH}_3)_2\text{Cl}$), from which silver chloride can be reprecipitated by adding an excess of nitric acid.

The **bromide** (AgBr) and **iodide** (AgI) are analogous to silver chloride in their properties and methods of formation. The bromide is pale yellow, and the iodide is yellow. They are used in photography (§ 491).

The formation and properties of silver chloride constitute the **test for silver** (compare § 136).

491. Photography. — This operation is based mainly on the fact that silver salts, especially the bromide and iodide, darken when exposed to the light. There are four steps.

1. **Exposing.** The photograph is taken on a glass plate, or a film, coated on one side with a thin layer of gelatin containing very fine grains of silver bromide. The plate or film is quickly exposed in the camera. The light that comes from the object passes through the lens, forms an image on the plate or film, and changes the silver salt in proportion to the intensity of the light reflected from the object.

2. **Developing.** The plate or film is immersed in a solution of a mild reducing agent, called a developer, *e.g.*, hydroquinone, pyrogallol acid, or special mixtures. As the developer acts upon the silver salt on the plate or film, the image gradually appears. This is a deposit of finely divided silver which varies in thickness in proportion to the light that fell upon the plate or film, being thickest where the light was most intense.

3. **Fixing.** The image is fixed by dissolving away the unchanged silver salt with a solution of sodium thiosulfate (or "hyposulfite"), and then washing the plate or film thoroughly in running water. On the fixed plate the dark parts of the object appear light and the light parts dark; the plate in this condition is called a negative (Fig. 218, left).

4. **Printing.** The print, or photograph, is made on paper coated with a mixture much like the one on the plate, though less sensitive to

light. The paper is laid upon the negative and both are exposed to the light so the light will pass through the negative first. Since the negative obstructs the light in proportion to the thickness of the silver deposit, the dark and light parts are reversed and a positive is obtained, *i.e.*, a photograph which has approximately the same shading as the object (Fig. 218, right).

On some kinds of paper the image appears at once, but on others it must be developed and fixed. Subsequent treatment called **toning** produces special results.



FIG. 218. — Daguerre — a pioneer in photography (negative (left) and positive (right)).

GOLD

492. History of gold. — Gold, like silver, is one of the oldest metals. For ages it has been the most highly prized of the metals and extensively used for personal adornment. The Latin name of gold, *aurum*, gives the symbol Au.

For several centuries the mediæval chemists, or alchemists, practiced alchemy, *i.e.*, they tried to produce gold by the transmutation of base or cheaper metals.

493. Occurrence of gold. — Its native compounds are few and rare. It is never found pure, being alloyed with silver and occasionally with copper or iron. It is disseminated in

fine, almost invisible, particles among ores of other metals, though not so abundantly as silver. Much gold is found in veins of quartz, and in the sand formed by the disintegration of gold-bearing rocks.

494. Mining and metallurgy of gold. — Gold was formerly mined by washing the gold-bearing sand in large pans or cradles. Now the sand is scooped up by huge dredgers and washed by machines. In **placer mining** and **hydraulic mining**, streams of water wash away the

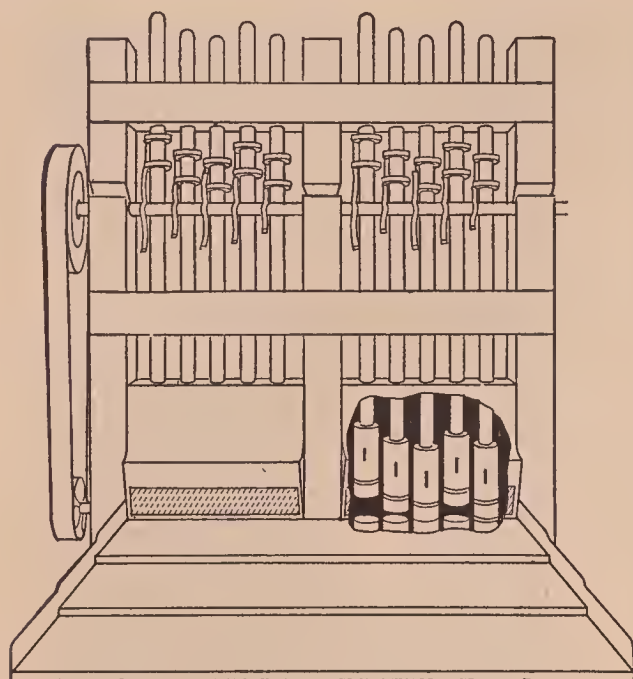


FIG. 219. — Stamp mills for crushing gold ore to a fine powder. Cut away on the right to show stamps (2 and 5 are lifted). Crushed ore passes through sieve on the left and the gold is caught by mercury on the plates (front). The rocky refuse is washed away.

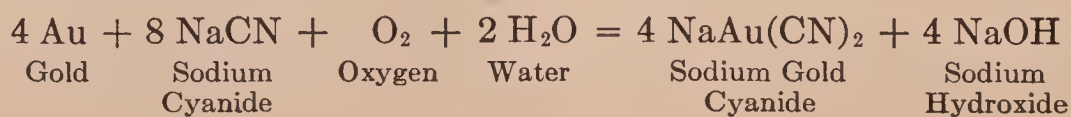
gold-bearing earth into long troughs or sluiceways. The lighter particles are washed away and the heavy particles together with the gold sink to the bottom where they are caught on cross bars. From this mixture, gold and silver are extracted with mercury (§§ 462, 477).

In **vein or quartz mining** the lumps of gold-bearing quartz are crushed to a fine powder in **stamp mills**, *i.e.*, in a row of huge iron mortars by hard pestles (Fig. 219). The moistened mass is floated over copper plates coated with mercury, which collects or dissolves about 50 per cent of the gold. The amalgam is heated, as in the metallurgy of silver, to remove the mercury, and the gold is extracted from the residue. The rest

(“tailings”) of the gold which is left in the slime is often extracted by the cyanide process (see below).

In the **chlorination process** the ore is treated with water containing chlorine or with bleaching powder and sulfuric acid; this operation forms a soluble gold chloride (AuCl_3), from which the gold is precipitated as a fine powder.

In the **cyanide process** the ore, usually low grade, or the slime from a previous extraction, is mixed with a weak solution of sodium cyanide and exposed to the air; this operation changes the gold into a soluble cyanide, thus: —



The gold is separated from this solution by electrolysis or by precipitation.

495. Refining gold. — Refining is accomplished by electrolysis. In one method, which is used in the United States mints, the solution in the cell is a mixture of gold chloride and hydrochloric acid, the anode is an alloy of silver and gold — rich in gold, — and the cathode is a thin sheet of pure gold. Gold is deposited on the cathode, and the silver forms silver chloride around the anode (Fig. 220).

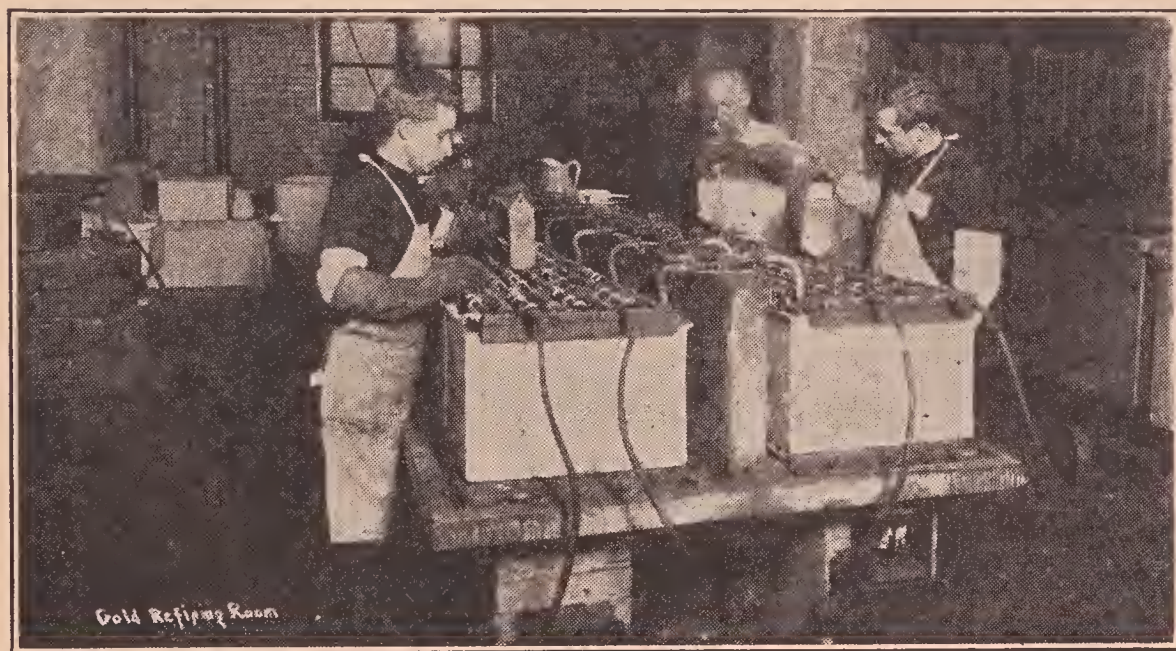


FIG. 220. — Purefying gold in the assay laboratory in New York City.

The purity of gold is expressed in **carats**. Pure gold is 24 carats fine. An alloy, for example, containing 22 parts of gold and 2 parts of copper is 22 carat gold.

496. Properties of gold. — Pure gold is a yellow metal but the color of commercial gold varies with the alloying metal. It is the most ductile and malleable of all the metals. The leaf into which it can be beaten is very thin. In some cases 110,000 leaves have a thickness of only 1 centimeter. Gold is one of the heaviest metals, its specific gravity being about 19.3. It forms alloys with many metals; most "gold" is an alloy — some is not gold at all!

Air, oxygen, hydrogen sulfide, and most acids do not attack it, and for this reason it is sometimes called a **noble**

metal. It is changed into gold chloride (auric chloride, AuCl_3) by chlorine (§ 135). With sodium cyanide, as described in § 494, it forms sodium gold (aurous) cyanide ($\text{NaAu}(\text{CN})_2$).

497. Uses of gold. — Pure gold is too soft for use as jewelry or coins, and it is usually alloyed with copper or silver. Gold coins contain gold and copper (§ 458). The United States standard gold coins contain 90 per cent gold and 10 per cent copper. Gold leaf of various grades is used to ornament books and signs. Jewelers use gold for many purposes; such gold varies from 12 to 22 carats in purity, though 14 or 18 carat gold is commonly used.

498. Gold compounds. — Gold forms two series of compounds — aurous and auric, in which the gold has the valence of + 1 and + 3 respectively. **Auric chloride** (AuCl_3) in dilute solution is reduced by stannous chloride solution to a beautiful purple precipitate; the latter is called “purple of Cassius,” and is colloidal gold. Its formation is the **test for gold**. In gold plating, which is much the same as silver plating, the solution contains the potassium gold cyanides ($\text{KAu}(\text{CN})_2$ and $\text{KAu}(\text{CN})_4$).

EXERCISES

1. Prepare a summary of the metallurgy of (a) silver and (b) gold.
2. Describe in order the steps in taking a photograph.
3. How is gold purified? What is 14 carat gold?
4. Prepare a summary of the properties of (a) silver and (b) gold.
5. Complete and balance: $\text{Ag}_2\text{SO}_4 + \text{KBr} = \text{K}_2\text{SO}_4 + \text{---}$.

Write the final equation in ionic form.

PROBLEMS

1. Calculate the weight of (a) silver in 1 kg. of silver nitrate and (b) gold in 1 gm. of potassium auricyanide.
2. How many grams of gold in a 14-carat ring which weighs 14 gm.?
3. (a) What weight of silver can be obtained from an American ten-cent piece which weighs 2.44 gm.? (b) How much gold from an American gold coin weighing 3.75 gm.?

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

Exercises S11 II (b) (1)	— Test for Chlorides.
Exercise *25 (c)	— Test for a Chloride.
Exercise *26	— Insoluble Chlorides (Silver part only).
Exercise 22 II (d)	— Test for Hydrogen Chloride.
Exercise 23	— Aqua Regia — T.
Exercise S33 (a)	— Testing for Ions.
Exercise S46 (c)	— Test for a Bromide.
Exercise S50 (d)	— Test for an Iodide.
Exercise S56 K	— Test for Gold.
Exercise S59 (b)	— Testing Salts.
Exercise S60	— Silver Salts and Photography — T.
Exercise S62	— Qualitative Analysis.

TOPIC XXV: ALUMINUM — CLAY AND CLAY PRODUCTS

499. Occurrence of Aluminum. — About 8 per cent of the earth's crust is combined aluminum; in abundance it ranks first among the metals and third among the elements (§ 325). All important rocks (except limestone and sandstone) and many rock-forming minerals are salts of silicic acid in which aluminum is one of the metallic components. Among such minerals are feldspar, mica, and hornblende, which are constituents of the common rocks called granite and gneiss. Clay, which is formed by weathering rocks, is mainly aluminum silicate.

Corundum and emery are impure aluminum oxide (Al_2O_3). Bauxite is an aluminum hydroxide ($\text{H}_4\text{Al}_2\text{O}_5$); it is often colored red by iron oxide. Cryolite is sodium aluminum fluoride (Na_3AlF_6).

500. Manufacture of aluminum. — Aluminum is manufactured by the electrolysis of aluminum oxide (Al_2O_3). The purified oxide, which is prepared from bauxite, is dissolved in melted cryolite, and when the current passes, aluminum is deposited at the cathode. This process was discovered in 1886 by a young American chemist named Hall and perfected by him.

A sketch of the apparatus is shown in Fig. 221. An open iron vessel (C, C) lined with carbon is the cathode. Connection with the cathode is made at D. The anode consists of several graphite bars (A, A, etc.) attached to a copper rod, by which they can be lowered as the graphite is consumed (by the liberated oxygen).

The bottom of the box is first covered with cryolite, the anode is lowered, and the box is then filled with cryolite (to which calcium fluo-

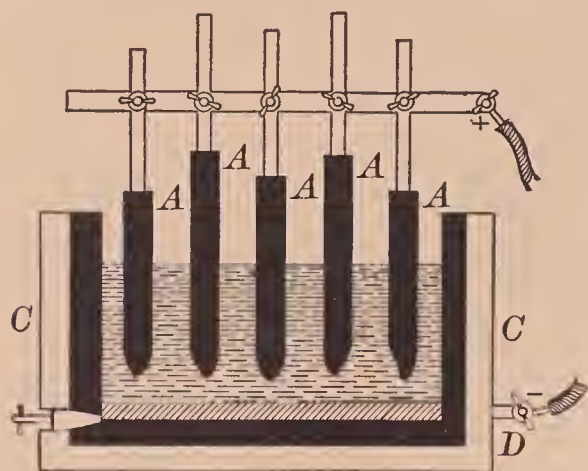


FIG. 221. — Sketch of the apparatus for the manufacture of aluminum by the electrolysis of aluminum oxide.

ride is added to lower the fusion point). When the current is turned on an arc is formed, and the resistance generates enough heat to melt the cryolite. Pure, dry aluminum oxide is now added, which dissolves in the cryolite and dissociates somewhat as electrolytes do in water. The oxygen goes to the anode and unites with the graphite. The graphite anodes are gradually lowered, and eventually have to be replaced.

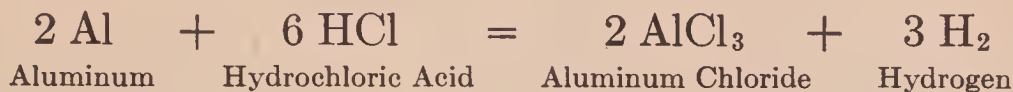
The aluminum sinks through the cryolite, and collects as a liquid at the bottom of the vessel.

The process is continuous, fresh aluminum oxide being added and the molten aluminum being drawn off at intervals. The cryolite and calcium fluoride are not decomposed as long as aluminum oxide is present. The aluminum produced is 98–99.5 per cent pure.

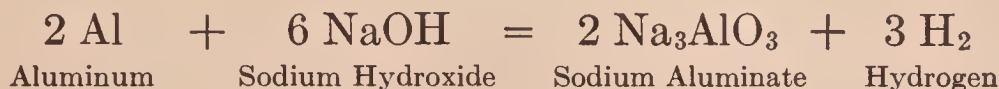
501. Physical properties of aluminum. — Aluminum is a lustrous white metal. It is the lightest of the common metals. Its specific gravity is only about 2.6 while that of iron is 7.8. It is ductile and malleable, and is extensively made into wire, rods, tubes, sheets, and foil (as thin as 0.0005 inch = 0.00127 cm.). It is a good conductor of heat and electricity. Compared with most metals, aluminum is rather hard and strong, being exceeded in this property only by iron and copper.

Aluminum melts at about 658° C. In the semi-molten state it can readily be extruded, *i.e.*, forced or pressed out through an opening into desired shapes. Just below the melting point it is brittle and can be ground into powder. Aluminum can be cast and welded, though it cannot be turned well in a lathe, nor can it be readily soldered to produce a permanent joint.

502. Chemical properties of aluminum. — Aluminum is very slightly tarnished by air, owing to the protecting film of oxide that forms on the surface. Hydrochloric acid reacts readily with it, thus : —



Under ordinary conditions nitric and dilute sulfuric acids do not affect it; concentrated sulfuric acid acts upon it, forming aluminum sulfate. It displaces many metals from their solutions, *e.g.*, copper (§ 462). Sodium chloride interacts with it, if dilute acids are present. With sodium and potassium hydroxides it forms aluminates and hydrogen, thus : —



503. Uses of aluminum. — The varied properties of aluminum, especially its strength, lightness, and durability, adapt it to numerous uses, *e.g.*, parts of military outfits, caps for jars and bottles, surgical instruments, tubes, fittings of boats, automobiles, and airships (using about one third of the production), parts of opera glasses and telescopes, framework of cameras, stock patterns for foundry work, hardware samples, scientific apparatus, and large vessels for chemical processes (Figs. 222, 223). Aluminum cooking utensils are extensively used.

Its silvery appearance and durability lead to its extensive use as an ornamental metal, both in interior decorative work and as numerous small objects. Aluminum leaf is used to letter book covers and signs, and the foil is used as a wrapper for food, candy, and tobacco. The powder suspended in an adhesive liquid forms a paint for steam pipes, radiators, storage tanks, smokestacks, and other metal objects exposed to heat or the weather.

Large quantities of aluminum are consumed in purifying steel, *i.e.*, removing air bubbles from the molten steel, thereby preventing the formation of small holes ("blow holes") in the castings.

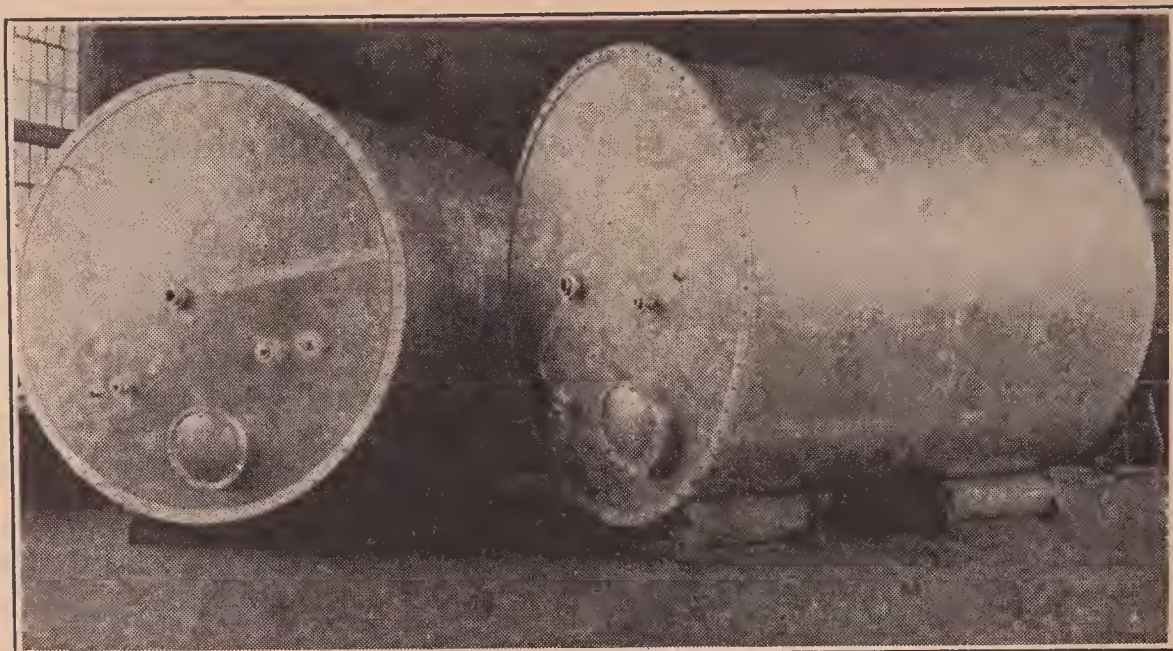


FIG. 222. — Aluminum tanks used in chemical plants. Each tank holds about 6000 gallons.

504. Alloys of aluminum. — Aluminum forms useful alloys, those with copper being the most important. The proportions of aluminum vary widely (from 5 to 95 per cent), thus giving a great variety of alloys. Those containing from 5 to 10 per cent of aluminum are called **aluminum bronze**. They have a golden luster, are readily melted, and are highly resistant. They have many uses. Those containing 90

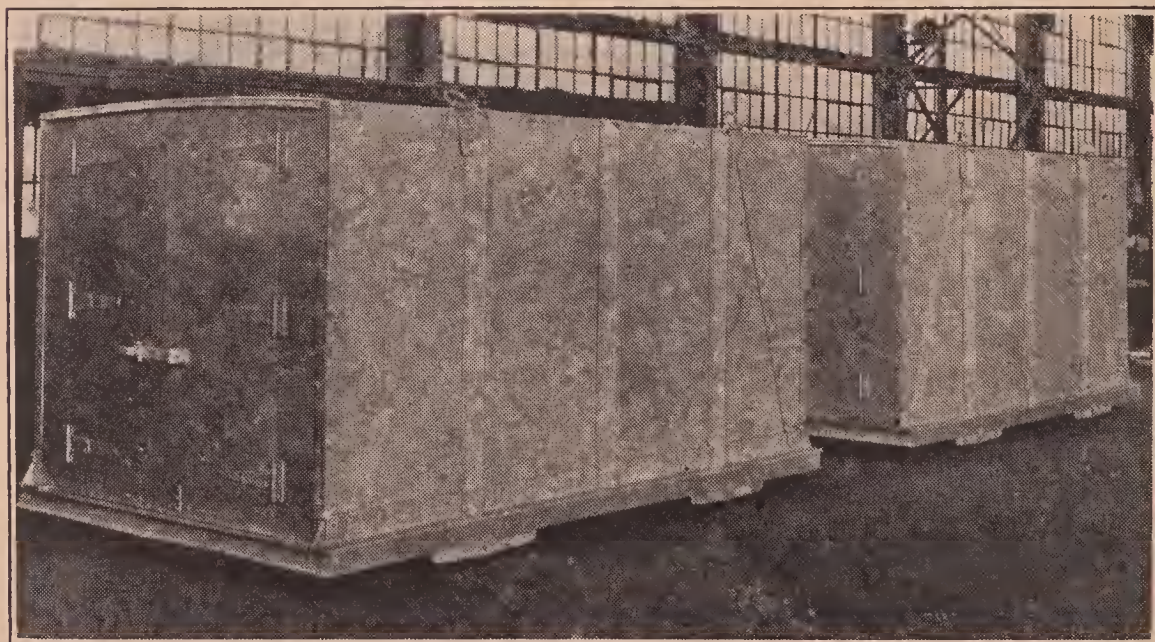


FIG. 223. — Large containers made of aluminum for shipping liquids which attack other metals.

to 95 per cent of aluminum are called **duralumin** and are the aluminum of the trade. They are silver-white. These alloys are used in making castings and household ware. The framework of airships is duralumin (Fig. 224).

An alloy with magnesium, called **magnalium**, contains from 75 to 90 per cent of aluminum. It is hard, light, attractive, and durable, and is used as parts of chemical balances and scientific instruments.

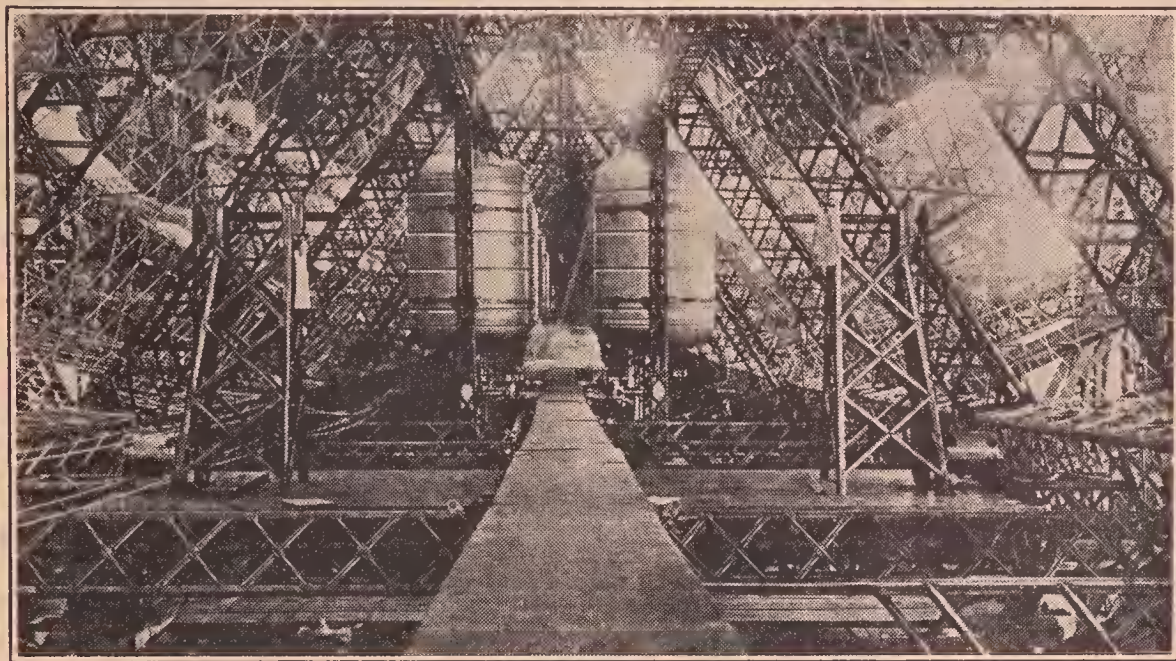


FIG. 224. — View of part of the interior of the airship *Los Angeles* showing the framework made of duralumin.

505. Thermit. — Aluminum is a powerful reducing agent. This property is utilized in the manufacture of certain metals and in welding.

When a mixture of chromium oxide, for example, and powdered aluminum is ignited at one point, the reduction proceeds rapidly throughout the mixture and the intense heat fuses the chromium, which can be removed from the crucible in a lump; the aluminum oxide rises to the top of the metal as a slag. The equation is: —



Other metals, *e.g.*, manganese, titanium, molybdenum, and tungsten, hitherto rare or expensive, are similarly prepared.

If a mixture of ferric oxide (Fe_2O_3) and powdered aluminum is ignited by a special mixture, a violent reaction occurs. The oxide is reduced to iron, which is melted by the intense heat (3000°C.) and protected by the layer of molten aluminum oxide. By using a special form of apparatus the molten iron can be conducted from the crucible into a mold around a joint or fracture (Fig. 225). This method is quick and

effective and is widely used to weld steel rails and repair fractures in machinery.

Mixtures of aluminum and oxides, used for this purpose, are called **thermit**, and the method is known as the **alumino-thermic** method.

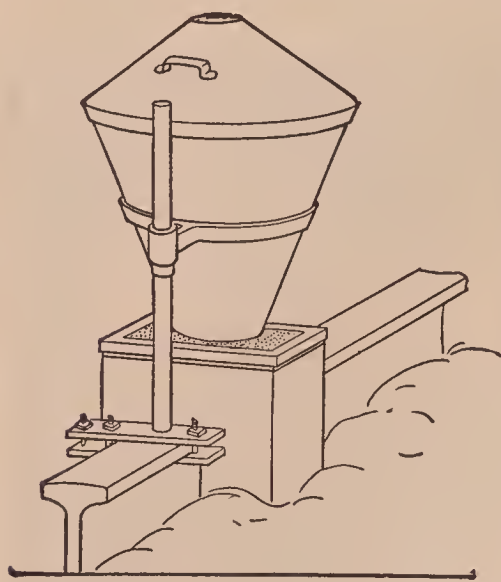


FIG. 225. — Sketch of a crucible and mold in position for welding a steel rail with thermit.

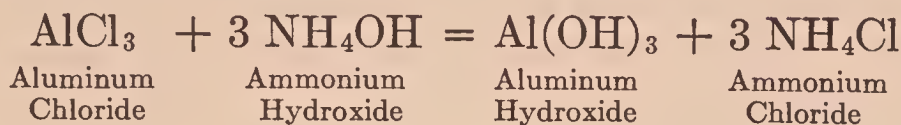
506. Aluminum oxide. — This is the only oxide of aluminum (Al_2O_3). It is often called **alumina**. Its native forms are **corundum** and **emery**. Both are very hard substances, pure corundum ranking next to diamond.

The transparent varieties of corundum have long been prized as gems, among them being the sapphire and ruby. The alumina which is manufactured from bauxite is a white, powdery substance.

Emery was formerly used as an abrasive. But it has been largely replaced by an artificial oxide called **alundum**. This product is manufactured by heating alumina in an electric furnace. On cooling, the mass forms a hard solid which is extensively used as an abrasive. Without abrasives like alundum and carborundum (§§ 51, 447) many modern industries, *e.g.*, automobile and airplane, would be well-nigh impossible.

When alumina, or any other compound of aluminum, is heated on charcoal with a blowpipe, then cooled, moistened with cobaltous nitrate solution, and heated again, the mass turns a beautiful blue color. This is a **test for aluminum** (compare § 474).

507. Aluminum hydroxide. — This is a white, jellylike solid formed by adding ammonium hydroxide to a solution of an aluminum salt, thus : —

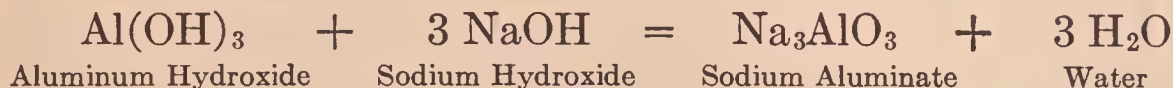


Aluminum hydroxide is an example of a gelatinous colloid or gel (§ 446). It is insoluble in water, but it dissolves in strong acids and strong bases (in excess), forming respectively aluminum salts and aluminates.

Aluminum hydroxide has weak basic and acid properties (compare § 472). An equation illustrating the basic property is : —

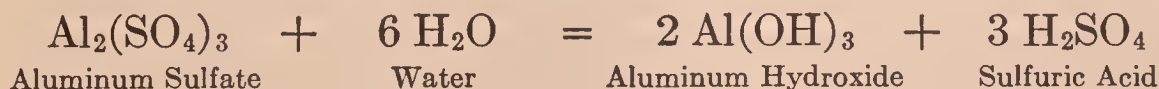


One illustrating the acid property is : —



508. Aluminum sulfate. — This is a white solid prepared from clay or bauxite by heating with sulfuric acid. The crystallized salt has the formula $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$. It is used as a mordant in dyeing and as an ingredient of the mixture (called size) put on paper to prevent ink from spreading.

A solution of aluminum sulfate has an acid reaction on account of hydrolysis (§ 281); the equation for the hydrolysis is : —



Practical application of this reaction is made in purifying water. Upon adding aluminum sulfate and lime to impure water, the gelatinous aluminum hydroxide that is precipitated slowly settles and carries with it suspended particles and bacteria (§ 81).

509. Alums. — A mixture of concentrated solutions of aluminum sulfate and potassium sulfate deposits crystals of

potassium alum or simply alum (Fig. 226). Its formula is $K_2Al_2(SO_4)_4$ or $K_2SO_4 \cdot Al_2(SO_4)_3$. It is the type of a class of similar salts called **alums**, which can be prepared by mixing sulfates of univalent and trivalent metals (*e.g.*, K, Na, NH_4 , and Al, Cr, Fe). For example, chrome (or chromium) alum is $K_2SO_4 \cdot Cr_2(SO_4)_3$.

Alums are rather soluble in water, and their solutions have an acid reaction owing to hydrolysis (§ 281). They crystallize as octahedrons (Fig. 226) and contain twenty-four molecules of water of hydration.

Alum (and sometimes aluminum sulfate) is an ingredient of alum baking powders (§ 283); the acid needed to liberate carbon dioxide is formed by the hydrolysis of the alum.

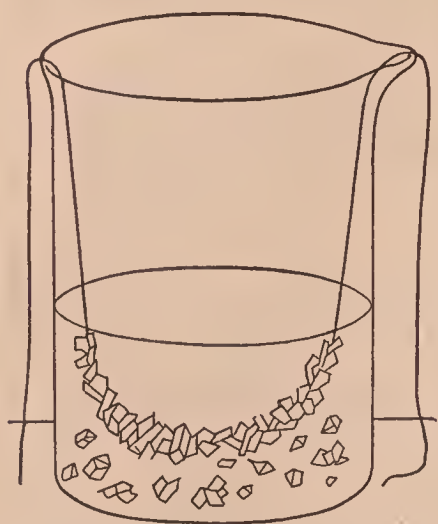


FIG. 226. — Alum crystals deposited from a concentrated solution.

Alums are used in dyeing and printing cloth, in tanning and paper making, as a medicine, for hardening plaster, in fireproofing wood and cloth, and in preparing aluminum compounds. Aluminum sulfate is displacing alum for many purposes, especially the purification of water.

510. Mordants. — Aluminum hydroxide is extensively used as a mordant in dyeing. Some fibers, *e.g.*, cotton, do not take up, or adsorb, a dye readily. Hence to prevent the dye from being washed off, a substance called a mordant is added to fix the dye within the fiber. Gelatinous colloidal hydroxides of aluminum (§ 507), iron, tin, and chromium are used.

The cloth to be dyed is first impregnated with an aluminum salt, such as aluminum acetate, and then exposed to steam. This operation changes the aluminum salt into aluminum hydroxide, which is precipitated in the fiber of the cloth. The mordanted cloth is next passed through a vat containing a solution of the dye, which is adsorbed by the aluminum hydroxide, forming a colored compound. The latter is relatively insoluble and cannot be easily washed from the cloth, *i.e.*, it is a fast color.

Dyes of this kind are called mordant or adjective dyes. They differ from (a) insoluble dyes like indigo which are precipitated within the fibers, and (b) direct or substantive dyes which produce colors in the fabric without mordants.

511. Clay. — This is a more or less impure aluminum silicate, formed by the slow decomposition of rocks containing aluminum compounds, especially the feldspars. Pure, typical feldspar is potassium aluminum silicate (KAlSi_3O_8). The products of its decomposition are chiefly an insoluble aluminum silicate and a soluble alkaline silicate. The latter is washed away. The pure aluminum silicate which remains is **kaolin** ($\text{H}_4\text{AlSi}_2\text{O}_9$ or $\text{H}_2\text{Al}_2(\text{SiO}_4)_2 \cdot \text{H}_2\text{O}$). Usually kaolin is mixed with particles of mica and quartz, calcium and magnesium carbonates, and iron compounds — the last giving the colors. This mixture, which varies in composition, is known as clay.

Kaolin undergoes hydration when mixed with water and finally acquires marked colloidal properties. In this so-called plastic state, the colloidal suspension is rather permanent and can be molded into various objects which retain their shape when dry. When heated, it loses its water of hydration, and does not melt (except at a very high temperature), but becomes a permanently hard mass without plasticity. These two properties (plasticity when wet and hardness when heated) are the foundations of the ceramic industries.

For ages porcelain and china have been made by mixing kaolin (free from iron), fine sand, and powdered feldspar, shaping the mass into the desired form by molds or on a potter's wheel, and then heating ("firing") in a kiln to a high temperature (Fig. 227). The mass when cool is hard and translucent (if thin), but porous. It is called *bisque*. To make it impervious to gases and liquids, its surface must be glazed. This is done by dipping it into a creamlike mixture of feldspar and silica, similar to that used for making the porcelain but more easily fused, and then heating it again. The thin coating melts, runs over the surface, penetrates the porous mass and fuses with it to some extent, and when cold finally forms a shiny, impervious glaze.

In making pottery the raw materials are less carefully selected and prepared, and not heated to such a high temperature. The best grades can hardly be distinguished from porcelain, but usually pottery is much heavier and thicker.

If less pure, plastic clay is used and heated to a moderate temperature, the product is known as **earthenware or stoneware**. This is a large class and includes tiles, terracotta, jugs, and flowerpots. This ware is porous and is sometimes glazed by throwing salt into the kiln just before the operation is over. The salt forms a fusible sodium aluminum silicate



FIG. 227. — Interior of a chemical porcelain factory.

upon the surface. The special grades of stoneware for use in chemical plants are made by a more careful procedure.

Clay products used for construction include bricks, drain pipe, etc. They are made from impure clay and heated just enough to harden the mixture. The product varies with the clay, but is often colored red owing to iron oxide formed from the iron compounds in the unburned clay. Buff bricks are made from clay containing a small proportion of iron. Fire bricks and other material designed to withstand high temperatures are made from clay containing considerable silica.

EXERCISES

1. Starting with aluminum how could you prepare in succession AlCl_3 , $\text{Al}(\text{OH})_3$, Na_3AlO_3 , AlCl_3 , $\text{Al}(\text{OH})_3$, Al_2O_3 , Al ?
2. Describe the manufacture of aluminum.

PROBLEMS

1. Calculate the weight of aluminum in (a) 20 gm. of aluminum oxide, (b) 34 gm. of aluminum hydroxide.
2. What weight of aluminum can be obtained from 100 kilograms of bauxite (93 per cent $\text{Al}(\text{OH})_3$)?

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

Exercise S12 (c) — Purification of Water — T.

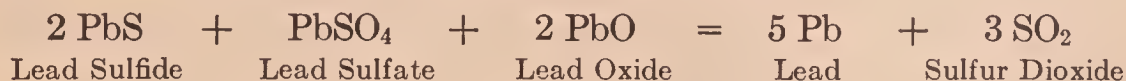
Exercise *16 — Effect of Shape on the Solubility of a Solid — T.

- Exercise S18 — Equivalent Weight of Aluminum.
 Exercise 56 (*g*) — Testing Baking Powders.
 Exercise S56 A — Tests for Metals (Aluminum).
 Exercise S58 (*a*) — Cobalt Nitrate Tests (Aluminum).
 Exercise S61 — Preparation and Properties of Aluminum Hydroxide.

TOPIC XXVI: LEAD

512. History of lead. — Lead and its compounds have been used since the dawn of history. The Chinese have used it for ages to line chests in which tea is stored and transported. The Romans, who obtained it from Spain, called it *plumbum nigrum*, i.e., black lead, and used it for conveying water just as we do today. The symbol Pb comes from the Latin word *plumbum*.

513. Metallurgy of lead. — Lead is obtained from galena (PbS) — the most abundant ore — by first roasting the ore to change part of the sulfide to the oxide and the sulfate. Then the air is excluded and the temperature raised; the mixture reacts thus: —



Lead produced by this process is impure and must be refined. The impurities make the lead hard and unfitted for most uses. There are two processes of refining.

1. The **Parkes process** is described in § 483, 2. The refined lead, left in the kettles, is cast into molds by machinery.

2. In the **electrolytic process** the cathode is a sheet of pure lead, and the electrolytic solution is a mixture of lead fluosilicate (PbSiF₆) mixed with gelatin. The anode is a slab of the impure lead. When the current passes, pure lead is deposited on the cathode and the other metals remain attached to the remnant of the anode or sink to the bottom.

514. Physical properties of lead. — Lead is a blue-gray metal. When scraped or cut, it has a brilliant luster, which soon disappears, owing to the formation of a film of oxide or of basic carbonate. It is so soft it can be scratched with the finger nail and rubbed off as black particles. It discolors the hands, and when drawn across a rough surface it leaves a black mark. For this reason it is sometimes erroneously called black lead (§ 40).

Lead is not tough nor very ductile. But it is malleable, and can be rolled into sheets and pressed (while just below the melting point) into pipe. It is a heavy metal, its specific gravity being 11.4; with the exception of mercury, it is the heaviest of the familiar metals. It melts at 327°C .

515. Chemical properties of lead. — Lead when heated strongly in air changes into oxides (mainly litharge, lead monoxide, PbO). Hydrochloric and sulfuric acids have little effect upon compact lead. Nitric acid produces lead nitrate ($\text{Pb}(\text{NO}_3)_2$).

In the presence of air, weak acids like acetic acid (or vinegar) and acids from fruits and vegetables change it into soluble, poisonous compounds. Soft water containing air, carbon dioxide, ammonia, nitrates, or chlorides, dissolves lead; and lead pipes should not be used to convey rain water or water containing ground gases. Permanently hard water (§ 298) usually forms a hard coating and thus prevents further action. All lead salts are poisonous, and ultimately cause serious illness.

Certain metals, *e.g.*, zinc and iron, precipitate lead from its solutions as a grayish mass, which often has a beautiful treelike appearance (§ 462).

516. Uses of lead. — Lead is extensively used as pipe. Lead pipe is not only used to convey water to and from parts of buildings, but also as a sheath for electric wires, both overhead and underground. Sheet lead is used to cover roofs and to line sinks, cisterns, and the cells employed in some electrolytic processes. The lead chambers and some evaporating pans used in manufacturing sulfuric acid are made of sheet lead. Shot and bullets are lead (alloyed with a little arsenic to make them hard). Spongy lead is used in preparing the plates of storage batteries. Lead wool (very fine wire) is used to calk pipe joints.

Lead is used to make many useful alloys, which as a rule are harder than lead. Those containing considerable lead are type metal (lead, tin, antimony), solder (lead and tin), Britannia and Babbitt metals, and pewter (§ 416). Solder melts at a lower temperature than lead and can be poured around a lead joint. Fusible metals contain lead (§ 417).

517. Lead oxides. — The **monoxide** (PbO) is a yellowish powder known as **massicot**, or a buff-colored crystalline mass called **litharge**. It is formed by heating lead in a current of air. It is made this way, though considerable is obtained as a by-product in separating silver from lead (§ 513). Large quantities are used in manufacturing some oils and varnishes, flint glass, a glaze for pottery, and as the source of many lead compounds.

The **tetroxide** (red lead or minium, Pb_3O_4) is a red powder, varying somewhat in color and composition. The pure compound has the composition represented by the formula Pb_2PbO_4 , *i.e.*, lead plumbate. It is prepared by heating lead or lead monoxide at the right temperature (about 450°C ., but not over 545°C .). It is used in making flint glass. Pure grades are made into artists' paint, but the ordinary grade, if mixed with the proper oil, is used to paint structural iron work (bridges, fences, gasometers, etc.), hulls of vessels, and agricultural implements. A mixture of linseed oil and red lead is used by plumbers and gas fitters to make joints tight. **Orange mineral** has about the same composition as red lead, though its color is lighter; its uses are the same.

The **dioxide** (PbO_2) is a brown powder formed by treating lead tetroxide with nitric acid or by the action of bleaching powder on sodium plumbite (Na_2PbO_2 , formed by dissolving lead hydroxide in sodium hydroxide). It is a strong oxidizing agent. Its formula is $\text{O}=\text{Pb}=\text{O}$. It is extensively used as the essential ingredient of the positive plate of electric storage batteries.

518. Lead carbonate. — This is obtained as a white powder by adding sodium bicarbonate solution to a solution of a lead salt. Sodium and potassium carbonates, however, produce a basic lead carbonate which has the composition corresponding to the formula $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ or $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$. It is known as **white lead** and is used extensively in the paint industry.

519. Paints. — A paint consists essentially of three ingredients: (a) a powder, (b) an oil, and (c) a filler. The powder, which is often called a pigment, is suspended in the oil, usually linseed oil, which hardens or "dries" (really oxidizes) to a tough film and sticks to a

surface. The powder, which is usually white lead (§ 520) with or without some colored substance, gives opacity, body, and color to the paint. It also fills the minute holes in the dried oil film and thereby assists in protecting the surface of the painted object from the action of oxygen and moisture. The filler is a white inert substance, *e.g.*, barium sulfate, or kaolin, added to fill in the pores and make the paint "go farther." Paint is often thinned with turpentine or oil just before using.

520. White lead. — This is a heavy, white powder which mixes well with linseed oil. It is the basis of many colored paints, pigments being added to give the desired color. White lead paint has a marked covering power, *i.e.*, it covers a surface well; it also dries to a good finish. But it darkens on exposure to hydrogen sulfide (which is often present in the air of cities) owing to the formation of black lead sulfide (PbS). In recent years other paint bodies, as the solids are called, have been mixed with, or substituted for, white lead, *e.g.*, zinc oxide (§ 471), kaolin, barium sulfate, and lithopone (a mixture of zinc sulfide and barium sulfate). These are

white solids which do not darken in the air, and they often improve the paint in other ways, *e.g.*, give it an impervious surface.

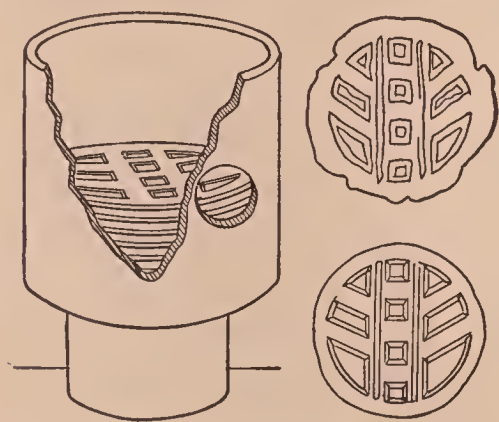


FIG. 228. — Earthenware vessel containing lead buckles to be made into white lead. Buckle before (*lower*) and after (*upper*) corrosion.

521. Manufacture of white lead. — White lead is manufactured by several processes.

1. In the **Dutch process**, perforated disks of lead, called buckles, are put in earthenware pots, which have a separate compartment at the bottom, containing dilute acetic acid (Fig. 228). These pots are arranged in tiers in a large building; spent tan bark is placed between each tier. The building is now closed except openings for the entrance and exit of air and steam. The fermentation of the tan bark produces carbon dioxide and moisture; heat is also liberated. The heat volatilizes the acetic acid, which changes the lead into lead acetate. The moist carbon dioxide converts the lead acetate into basic lead carbonate or white lead.

2. In **another process**, melted lead is blown ("atomized") into a very fine powder by a jet of steam, and the powder is beaten for several days with acetic acid, carbon dioxide, and air.

3. In a **third process**, white lead is precipitated by passing carbon dioxide into basic lead acetate solution.

522. Other lead compounds. — Native lead sulfide (PbS) is the mineral galena, the chief ore of lead. It resembles lead in appearance, but is harder and is usually crystallized as cubes, octahedrons, or their combinations (Fig. 229). It is obtained as a black precipitate by the interaction of hydrogen sulfide (or other soluble sulfides) and a solution of a lead salt. Its formation is a **test for lead**. The **chloride** (PbCl_2) is a white solid formed by adding hydrochloric acid, or a soluble chloride, to a cold solution of a lead salt. It dissolves in hot water (§ 136). The **sulfate** (PbSO_4) is a white solid, formed by adding sulfuric acid, or a soluble sulfate, to a solution of a lead salt. It is very slightly soluble in water, but

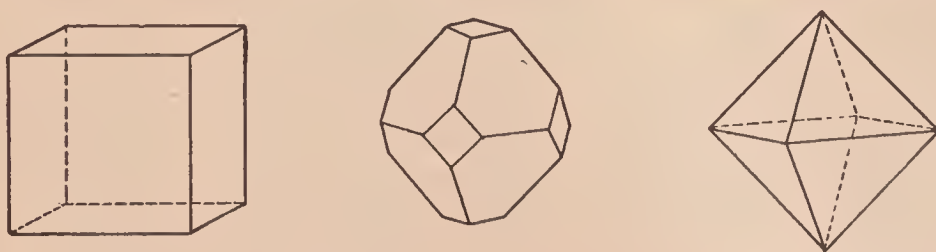


FIG. 229. — Galena crystals (cube, octahedron and cube, octahedron).

soluble in concentrated sulfuric acid, hence crude sulfuric acid sometimes contains lead sulfate. The white powder called “sublimed white lead” is about 75 per cent lead sulfate; it is used as a body for white paint. The **chromate** (PbCrO_4) is a yellow solid formed by adding a solution of a lead compound to a solution of potassium chromate or potassium dichromate. It is sometimes called chrome yellow and is used as a pigment in the paint industry. Its formation serves as a **test for lead**. The **arsenate** ($\text{Pb}_3(\text{AsO}_4)_2$) is a white solid, sparingly soluble in water; it is used as an insecticide for leaf-eating insects.

EXERCISES

1. Describe the metallurgy of lead.
2. Name three alloys which contain large proportions of lead. Name several alloys containing a minor proportion.
3. State the tests for lead.

4. Practical topics: (a) How would you test paint for lead? (b) What advantage has tin over lead for pipes? Lead over tin? (c) What is red lead? White lead? Black lead? (d) How would you show the presence or absence of lead in a lead pencil?

PROBLEMS

1. How many gm. of lead (a) in 200 gm. of galena, (b) in 1 kg. of litharge?
2. A cube of lead is 6 cm. on each edge. How much does it weigh?

SUGGESTIONS FOR LABORATORY WORK

(References are to Newell's Laboratory Exercises in Chemistry)

Exercise S3 (a)	— Preparation of Oxygen from Lead Dioxide.
Exercise 31 B (a), (b), (c)	— Insoluble Salts of Lead.
Exercise *47 (b)	— Test for a Sulfide.
Exercise *48 II (b)	— Test for a Sulfide.
Exercise S48 (b)	— Properties of Sulfides.
Exercise *53 B (a)	— Reduction of Lead Oxide.
Exercise *61 (b), (c)	— Displacement of Metals.
Exercise S56 G	— Tests for Metals (Lead).
Exercise S59	— Testing Salts (Lead part only).
Exercise S62	— Qualitative Analysis.
Exercise S62 (c)	— Tests for Lead.

TOPIC XXVII: RADIUM — RADIOACTIVITY

523. What is radium? — Radium is a metallic element, which is a constituent of rare uranium-bearing minerals. The richest deposits are in the Belgian Congo district of Africa, which is now the source of supply.

The proportion of radium in these minerals is only a few milligrams to the ton. But this small proportion is carefully extracted by a chemical process; the radium is then separated from the other metals as radium chloride or bromide by fractional crystallization.

The term *radium* as usually used means a compound, *e.g.*, the commercial salt is radium bromide (RaBr_2). The price of radium compounds is high, about \$75,000 a gram (of actual radium in the salt).

524. Discovery of radium. — About 1896, the French physicist Henri Becquerel discovered that uranium compounds affect a photographic plate in the dark or when wrapped in light-proof paper. Some minerals containing uranium compounds, particularly pitchblende, were later (1898) found by Madame Curie (Fig. 230) to be more active than uranium compounds. She studied pitchblende carefully, and subsequently in collaboration with her husband, Pierre Curie (1859–1906), extracted from this mineral a minute quantity of a new substance which was exceedingly active, many thousands of times more active than an equal weight of a



FIG. 230. — Madame Curie (1867–) in her laboratory.

uranium salt. Madame Curie gave the name radium to its elementary constituent.

525. General properties of radium and radium compounds. — Radium forms salts like those of calcium, *e.g.*, a soluble chloride (RaCl_2) and hydroxide ($\text{Ra}(\text{OH})_2$), and a relatively insoluble sulfate (RaSO_4) and carbonate (RaCO_3). Volatile radium compounds tinge the Bunsen flame red.

526. Radioactivity. — Besides the properties just enumerated, radium compounds have special properties which are conspicuously different from those of most substances. They are called radioactive properties. The term *radioactivity* is used to include these properties.

1. *Radium compounds spontaneously evolve considerable heat.* A radium salt is always from 3 to 5° C. warmer than



FIG. 231. — Dish of radium bromide photographed (by itself) in a dark room.

the surrounding air. It has been calculated that radium liberates enough heat every hour to raise a little more than its own weight of water from the freezing point to the boiling point. Moreover, this liberation of heat is kept up continuously.

2. *Radium compounds affect a photographic plate just as light does.* If a tube containing a radium compound is left a short time on a photographic plate wrapped in black paper, or if a dish con-

taining a radium compound is exposed to a plate in the dark, an image is produced when the plate is developed (Fig. 231).

3. *Radium compounds ionize the surrounding air, i.e., make it a conductor of electricity.* For example, radium compounds discharge an electroscope. An electroscope (Fig. 232) contains two thin strips (*D*, *E*) of gold or aluminum, which separate when the electroscope is charged with electricity. Radium compounds, if brought near a charged electroscope, ionize the air, which passes in at *A*, affects the charging rod *B*, and passes out at *C*. Thus it permits the escape of electricity from the electroscope, i.e., discharges the electroscope; hence the leaves (*E*, *D*) fall together.

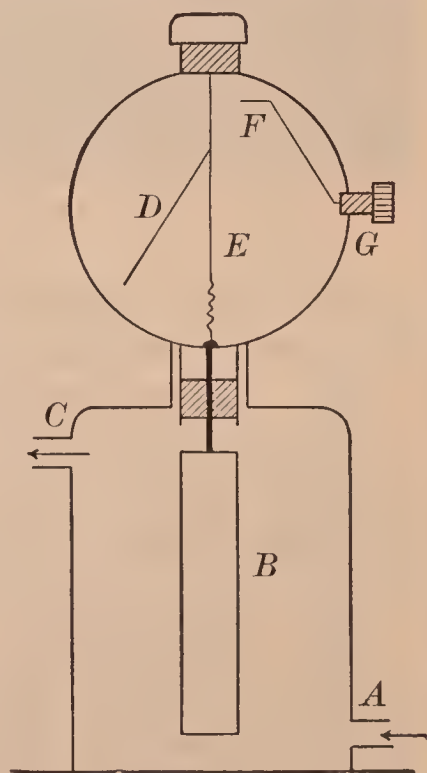


FIG. 232. — Sketch of an electroscope.

(The device G, F allows the electroscope to be charged or discharged.) The electroscope is used to detect radium compounds, and to determine the proportion of radium in mixtures.

4. *Radium compounds make certain substances luminous.* This is a conspicuous, and possibly the best-known property. Luminous watch, clock, and instrument dials, push buttons, door knobs, electric light chains, etc., consist essentially of a specially prepared crystalline zinc sulfide containing a minute quantity of a radium compound. (Sometimes a less expensive radioactive substance is used.)

During the World War radium mixtures were indispensable in making luminous dials for airplanes, submarines, gun sights, signs, etc. Tubes and other vessels containing radium compounds glow in the dark. In museums the visitor sometimes is guided by luminous arrows of radium paint through dark passageways into a small inclosure, where the radium compounds are seen glowing!

527. Interpretation of radioactivity. — It was first thought that radioactivity was due to rays or radiations; hence the name radium. Many interesting experiments prove, however, (1) that radioactivity is caused by the spontaneous emission of two kinds of electrically charged particles, called alpha (α) and beta (β) particles, and (2) that the emission of beta particles is accompanied by pulsations in the ether called gamma (γ) rays.

528. Alpha particles. — The alpha particles are positively charged and are shot off from the radioactive substance with great velocity — in some cases as great as 14,000 miles a second.

Each alpha particle carries two unit charges of positive electricity. Alpha particles are charged helium atoms (He^{++}). If deprived of their charges, they become helium atoms and the weight of each is four times that of a hydrogen atom. To the alpha particles are due many of the electrical phenomena of radioactive substances, *e.g.*, ionizing air.

Although alpha particles move very fast in straight lines, they do not travel very far. They are completely stopped by the time they have plowed through the air to a depth of

3 to 8 centimeters. They are almost entirely stopped by a thin sheet of paper and by aluminum leaf 0.1 mm. thick. The paths of alpha particles have been photographed as the particles shot through moist air (Fig. 233).

529. Beta particles. — The beta particles are electrons, *i.e.*, particles of negative electricity. They move in straight lines (at first) with great velocity, varying from 16,000 to 180,000 miles a second — the maximum being nearly as great as the velocity of light (186,000 miles a second). The beta particles are very light, their weight being about $\frac{1}{1845}$ of the weight of a hydrogen atom. The beta particles produce most of the photographic effect of radioactive substances. (Refer to §§ 357, 358, 424 for electrons.)

530. Gamma rays. — The gamma rays have the least ionizing and photographic power, but they are the most penetrating. They

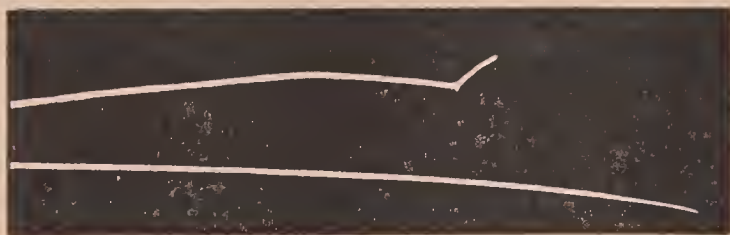


FIG. 233. — Path of alpha particles in moist air.

pass readily through thick layers of metal, *e.g.*, several inches of lead. Glass tubes containing radium salts are inclosed in thick lead vessels to

absorb the gamma rays. Gamma rays are not affected by a magnet; hence they have no electrical charges.

531. Radium and energy. — The heat, electrical, and light energy associated with radioactive substances is due to release of energy within the radium atom, resulting in an atomic disintegration and expulsion of fragments at a great velocity. Thus, the rapidly moving alpha and beta particles are suddenly stopped by the air, metals, and the radioactive solid itself, and heat and light result.

532. Uses of radium. — The products from radium, especially beta particles and gamma rays, have a powerful effect on living matter, and are utilized to cure certain skin diseases and abnormal growths. The radium compound itself is so expensive it is seldom used directly. One of the products of the disintegration of radium is radon. And since radon gives off gamma rays constantly, radon is used instead of the

radium compound. The radon is pumped off at stated intervals into tiny glass tubes which can be placed upon or within the flesh.

533. Radium is decomposing spontaneously. — Although radium is an element which possesses many properties like those of the other elements, it differs from most of the elements in being unstable. That is, radium is slowly disintegrating. One of the final products is the stable element lead.

Other products of the disintegration of radium atoms are produced, as shown in § 536. One product, *viz.*, radon (formerly called radium emanation and niton), is given off continuously by radium compounds. It condenses at the temperature of liquid air and glows in the dark; by raising the temperature, the gas can be recovered by blowing air through the tube. It belongs to the same group of elements as helium and argon, and has properties much like those of argon (§ 419). Radon is an unstable gas, and gives helium as one product.

Since the two elementary gases, helium and radon, are produced spontaneously from all radium compounds, the radium atom itself must be disintegrating spontaneously. This means that the atom of one element (radium) is transforming itself into the atoms of two other elements (helium and radon). But unlike other chemical transformations, the decomposition of the radium atom cannot be hastened or retarded by the chemist. It goes on unceasingly and unvaryingly at temperatures between liquid air and the electric furnace.

Furthermore, this transformation means that the element radium is slowly disappearing. The change is not rapid. Experiments show that half of a given weight of radium would disappear in about 1700 years, half of the residue in another 1700 years, and so on. Radon is also disintegrating. Its rate, however, is rapid; the half period, as it is called, is about 4 days.

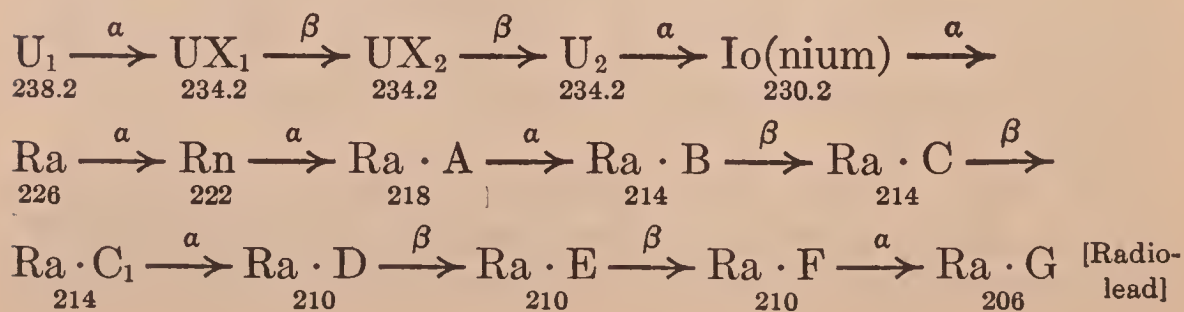
534. The radium disintegration series. — As intimated above, helium and radon are not the only elements formed by the disintegration of radium. There are at least eight others,

all rather unstable and short-lived, except one (radium—G, or radio-lead). Radium itself is a product of the disintegration of uranium. Uranium, the heaviest of all the elements, is regarded as the parent substance in the radium disintegration series. The others in the series are given in § 536. All are elements; some are very unstable, the half period being only a few minutes. Helium is not a member of the series, but is given off in some of the transitions. Electrons are also expelled in some cases. The final product of this disintegration series is radio-lead (§ 536).

535. Some points of the theory of radioactive disintegration. — We have already stated (a) that radium compounds are continuously giving off alpha and beta particles and gamma rays, (b) that the process of radioactive change is the result of a spontaneous disintegration of the atoms of radium, and (c) that radioactive changes are independent of external conditions (*e.g.*, temperature) and the kind of chemical compound, and proceed at a definite rate. Hence it is concluded that radioactivity is a property of the atom itself.

Radioactive changes involve not only the production of elements but the expulsion of alpha and beta particles, *i.e.*, the loss of a charged helium atom and an electron. An electron has a negligible weight, but a helium atom has the weight 4. Hence the loss of an electron leaves the weight of an atom unchanged, whereas the expulsion of a helium atom lowers an atomic weight by 4 units.

536. Transformations in the uranium series. — The changes in this series are shown in the following scheme, which includes the symbol and atomic weight of each element, and the kind of particle emitted (α = alpha particle and β = beta particle or electron).



Let us glance at two examples.

1. In passing from uranium to radium, three helium atoms are lost. Therefore, the atomic weight of radium should be 12 units (3×4) less than uranium. From the scheme we see that uranium has the atomic weight 238.2 and radium 226.

2. Eight helium atoms are lost in passing from uranium to radium—G (the final product). Hence the final product in this series should have the atomic weight 206 (*i.e.*, $238.2 - (8 \times 4)$). The atomic weight of radio-lead was found to be 206.08 by exceptionally accurate experiments.

The atomic weight of lead from other (*i.e.*, non-radioactive) sources is 207.2, which is actually — not estimated — higher than that of radio-lead.

The two forms of lead have identical chemical properties, *e.g.*, form compounds exactly alike in exactly the same way. They differ only in atomic weight. Elements which differ in atomic weight but not in chemical properties are called **isotopes** or **isotopic elements**.

EXERCISES

1. Prepare a summary of (a) radium, (b) radioactivity, and (c) uranium disintegration series.
2. State the properties of (a) alpha particles and (b) beta particles.
3. State the uses of radium compounds.

PROBLEM

1. Calculate the weight of radium in 1 milligram each of (a) radium bromide, (b) radium nitrate, (c) radium sulfate.

APPENDIX

1. The pressure of water vapor in millimeters of mercury is : —

TEMPERA- TURE	VAPOR PRESSURE	TEMPERA- TURE	VAPOR PRESSURE	TEMPERA- TURE	VAPOR PRESSURE
12	10.5	17	14.4	22	19.7
12.5	10.8	17.5	14.9	22.5	20.3
13	11.2	18	15.4	23	20.9
13.5	11.6	18.5	15.9	23.5	21.5
14	11.9	19	16.4	24	22.2
14.5	12.3	19.5	16.9	24.5	22.8
15	12.7	20	17.4	25	23.6
15.5	13.1	20.5	18.0	25.5	24.3
16	13.6	21	18.5	26	25.0
16.5	14.0	21.5	19.1	26.5	25.7

The numbers in the Vapor Pressure columns are the values for a in formulas for the reduction of gas volumes, *e.g.*, the formula in § 348, last paragraph, and in the following condensed formula : —

$$V = \frac{V'(P' - a)}{760(1 + (0.00366 \times t))}$$

2. **Books.** — Starred (*) books are primarily for teachers, though many parts of these books are suitable for pupils.

1. **Alembic Club Reprints*. University of Chicago Press. Nos. 2 (Dalton, Atomic Theory), 3 (Cavendish, Air), 4 (Avogadro, Molecules), 6 (Davy, Alkalies), 7 (Priestley, Oxygen), 9 (Davy, Chlorine).

2. *Chemical Discovery and Invention in the Twentieth Century*. Tilden. E. P. Dutton & Co.

3. *Chemistry and Civilization*. Cushman. E. P. Dutton & Co.
4. *Chemistry Applied to Home and Community*. Beery. J. P. Lippincott Co.
5. *Chemistry in Agriculture*. Chamberlain. The Chemical Foundation (N. Y.).
6. **Chemistry in America*. Smith. D. Appleton & Co.
7. *Chemistry in the Home*. Howe and Turner. Charles Scribner's Sons.
8. *Chemistry in Industry*. Vols. I and II. Howe. The Chemical Foundation (N. Y.).
9. *Chemistry in the Service of Man*. Findlay. Longmans, Green & Co.
10. *Chemistry in the World's Work*. Howe. D. Van Nostrand Co.
11. *Coal and the Coal Mines*. Greene. Houghton, Mifflin Co.
12. **College Chemistry*. Newell. D. C. Heath & Co. Advanced book for reference.
13. *Discoveries and Inventions of the Twentieth Century*. Cressy. E. P. Dutton & Co.
14. **Elements of Industrial Chemistry*. Rogers. D. Van Nostrand Co.
15. *Essays in Historical Chemistry*. Thorpe. Macmillan Co.
16. **Experiments in College Chemistry*. Newell. D. C. Heath & Co. (Experiments based on No. 12.)
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Deacidified using the Bookkeeper process.
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Treatment Date: June 2013

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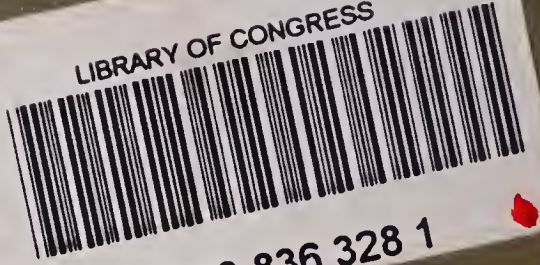
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**TABLE OF ELEMENTS, SYMBOLS, ATOMIC NUMBERS,
AND ATOMIC WEIGHTS**

ELEMENT	SYM- BOL	AT. No.	ATOMIC WEIGHT	AP- PROX. AT. WT.	ELEMENT	SYM- BOL	AT. No.	ATOMIC WEIGHT	AP- PROX. AT. WT.
Aluminum	Al	13	26.97	27	Mercury	Hg	80	200.61	200
Antimony	Sb	51	121.76	121.5	Molybdenum	Mo	42	96.0	—
Argon	A	18	39.94	40	Neodymium	Nd	60	144.27	—
Arsenic	As	33	74.96	75	Neon	Ne	10	20.183	—
Barium	Ba	56	137.36	137	Nickel	Ni	28	58.69	58.7
Beryllium	Be	4	9.02	—	Nitrogen	N	7	14.008	14
Bismuth	Bi	83	209.00	209	Osmium	Os	76	190.8	—
Boron	B	5	10.82	—	Oxygen	O	8	16.000	16
Bromine	Br	35	79.916	80	Palladium	Pd	46	106.7	—
Cadmium	Cd	48	112.41	—	Phosphorus	P	15	31.027	31
Calcium	Ca	20	40.07	40	Platinum	Pt	78	195.23	—
Carbon	C	6	12.000	12	Potassium	K	19	39.10	39
Cerium	Ce	58	140.13	—	Praseodymium	Pr	59	140.92	—
Cesium	Cs	55	132.81	—	Radium	Ra	88	225.97	226
Chlorine	Cl	17	35.457	35.5	Radon	Rn	86	222	—
Chromium	Cr	24	52.01	52	Rhodium	Rh	45	102.91	—
Cobalt	Co	27	58.94	59	Rubidium	Rb	37	85.44	—
Columbium	Cb	41	93.1	—	Ruthenium	Ru	44	101.7	—
Copper	Cu	29	63.57	63.5	Samarium	Sm	62	150.43	—
Dysprosium	Dy	66	162.46	—	Scandium	Sc	21	45.10	—
Erbium	Er	68	167.7	—	Selenium	Se	34	79.2	—
Europium	Eu	63	152.0	—	Silicon	Si	14	28.06	28
Fluorine	F	9	19.00	19	Silver	Ag	47	107.880	108
Gadolinium	Gd	64	157.26	—	Sodium	Na	11	22.997	23
Gallium	Ga	31	69.72	—	Strontium	Sr	38	87.63	—
Germanium	Ge	32	72.60	—	Sulfur	S	16	32.064	32
Gold	Au	79	197.2	197	Tantalum	Ta	73	181.5	—
Hafnium	Hf	72	178.6	—	Tellurium	Te	52	127.5	—
Helium	He	2	4.002	4	Terbium	Tb	65	159.2	—
Holmium	Ho	67	163.5	—	Thallium	Tl	81	204.39	—
Hydrogen	H	1	1.008	1	Thorium	Th	90	232.12	—
Indium	In	49	114.8	—	Thulium	Tm	69	169.4	—
Iodine	I	53	126.932	127	Tin	Sn	50	118.70	119
Iridium	Ir	77	193.1	—	Titanium	Ti	22	47.90	—
Iron	Fe	26	55.84	56	Tungsten	W	74	184.0	—
Krypton	Kr	36	82.9	—	Uranium	U	92	238.14	—
Lanthanum	La	57	138.90	—	Vanadium	V	23	50.96	—
Lead	Pb	82	207.22	207	Xenon	Xe	54	130.2	—
Lithium	Li	3	6.940	—	Ytterbium	Yb	70	173.6	—
Lutecium	Lu	71	175.0	—	Yttrium	Y	39	88.93	—
Magnesium	Mg	12	24.32	24	Zinc	Zn	30	65.38	65
Manganese	Mn	25	54.93	55	Zirconium	Zr	40	91.22	—

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